Characterisation of Potential Replacements for Nickel Compounds used in Decorative Chromium Plating

STACEY HINGLEY BSc

A thesis submitted in partial fulfilment of the
requirements of the University of Wolverhampton
for the degree of Doctor of Philosophy

This research programme was carried out in collaboration with the RPSRC,
MacDermid Plc and Kohlar Mira

November 2013

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ABSTRACT

The electroplating industries use soluble nickel salts in numerous applications. Over the past few years this has become problematic due to the reclassification of these salts from a harmful substance to now a toxic substance. The introduction of the legislation REACH (Registration, Evaluation, Authorisation & restriction of CHemicals) has meant the electroplating industry has had to use less harmful chemicals where possible, thus meaning companies are investing in research to find an alternative to the nickel deposit.

In this study, alternative deposits under investigation as a potential replacement to the nickel deposit under the decorative chromium deposit has been characterised in terms of the appearance, surface topography and corrosion resistance by using spectrophotometry, scanning electron microscopy (SEM), atomic force microscopy (AFM), linear polarisation, electrochemical impedance spectroscopy (EIS) and accelerated corrosion salt spray methods.

Spectrophotometry identified that a white Cu-Sn alloy gave a bluer appearance in comparison to the nickel deposit, when the chromium deposit was plated on top this modified the colour slightly giving the white Cu-Sn alloy with chromium a similar appearance to the nickel and chromium deposit. The yellow Cu-Sn alloy was yellow in colour with a visibly dull appearance, but when chromium was plated on top of the yellow Cu-Sn alloy the colour was improved but still remained dull.

The SEM and AFM results identified that the white Cu-Sn alloy deposit had similar nodulated topography to the nickel deposit and when the chromium was plated on top the topography changed only slightly. While the yellow Cu-Sn alloy deposits showed a more crystalline structure and increased roughness in comparison to the nickel deposit, the chromium deposit plated on top did not change the structure of the underlying deposit but it did reduce the roughness slightly.

Electrochemical corrosion tests showed the white Cu-Sn alloy to have a higher polarisation resistance compared to the nickel deposit, thus suggesting it would provide similar corrosion protection to the nickel deposit. The yellow Cu-Sn alloy proved to have a faster corrosion rate in comparison to the nickel deposit.

Accelerated corrosion tests proved the white Cu-Sn alloy to be more corrosive than the nickel despite the electrochemical test results, it was concluded that the white Cu-Sn alloy deposit was porous and therefore provided less corrosion protection to the substrate in comparison to the nickel deposit. The yellow Cu-Sn alloy had a lower corrosion protection than the nickel deposit and when combined as a duplex Cu-Sn alloy with the white Cu-Sn alloy deposit there was no improvement in corrosion performance. The plated chromium deposit did improve the corrosion protection for most deposits but none of the alternatives could match the corrosion protection offered by the standard nickel with chromium deposit.

This study concluded that the white Cu-Sn alloy with chromium deposit was found to be a potential alternative to the nickel with chromium deposit for applications

where appearance is primary, no alternative could be found to match the corrosion protection provided by the standard nickel and chromium process.

ACKNOWLEDGEMENTS

I would like to take this opportunity to show my appreciation to the University of Wolverhampton and the School of Technology department. I wish to thank my academic supervisors Prof. C. F. Oduoza and Prof. C. D. Williams and my industrial supervisors Dr T. Pearson and Dr P. Lansdell for their support and guidance throughout this study.

I wish to acknowledge the Engineering and Physical Science Research Council (RPSRC), MacDermid Plc and Kohlar Mira for their sponsorship and support, with thanks to Mr M. Thomson, MacDermid Plc for his guidance in electroplating the deposits required in this study.

The love and support my family and friends have given me throughout this study has been greatly appreciated, it has helped me keep focused and motivated and therefore I'm extremely grateful to them.

DEDICATION

This thesis is dedicated to my loving husband Jade Hingley for being my source of inspiration and his continued support and encouragement throughout our life together and to my gorgeous son Jensen Hingley whose smile and love completes our family.

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LIST OF ABBREVIATIONS

ACD	Allergic contact dermatitis
AFM	Atomic force microscope
CASS	Copper accelerated acetic acid salt spray
COMAH	Control of major accident hazards
COSHH	Control of substances hazardous to health
EIS	Electrochemical impedance spectroscopy
ELV	End of life directive
HSE	Health and safety executive
NSS	Neutral salt spray
PPE	Personal protective equipment
SEM	Scanning electron microscope

CHAPTER 1: INTRODUCTION

1.1 Background to research

The electroplating industry has been under intense pressure over the last few years due to numerous factors which include the increase in metal prices, economic climate and the new regulation, REACH (Registration, Evaluation, Authorisation & restriction of CHemicals). These factors have led the electroplating industry to find more economical and less harmful chemicals (Metal-Weekly 2004; REACH 2010).

Nickel metal has been in high demand over the last decade due to its versatile applications and use in a wide variety of industries including the electroplating industry. The electroplating industry uses soluble nickel salts to deposit nickel metal either by electrolytic or electroless methods. In one electrolytic application, nickel is used under decorative chromium to provide corrosion protection and a high quality finish. In 1996 an EU risk assessment was established to investigate nickel and its compounds with regards to its impact on both the environment and human health. One outcome of this was the reclassification of nickel in 2007 from its existing status of a harmful substance to now a toxic substance. The reclassification of nickel metal and four soluble nickel salts had led the electroplating industry to investigate alternatives and with REACH enforcing the use of less harmful chemicals where possible, the electroplating companies have begun to invest in research to find an alternative to the nickel deposit.

1.2 Problem statement

Soluble nickel salts are classified as a carcinogen by inhalation, this includes nickel chloride and nickel sulphate which are used in the electroplating industry. Nickel metal and soluble nickel salts are known allergens and cause allergic contact dermatitis (ACD) (Kwangsukstith 1995). The public are more likely to come into contact with nickel metal as opposed to nickel salts so the elimination of nickel will benefit both the public and the electroplater. Nickel is found naturally in the environment, nickel in the soil gets absorbed by plants and is introduced into the food chain, also it becomes dissolved in our drinking water so water companies monitor the nickel levels to keep within the UK/European limit of 40µg/l (Seven-Trent 2005).

The electroplated nickel is used under chromium to improve the quality of the finish and corrosion protection. The finish is improved by the nickel being able to level out scratches in the substrate, have good throwing power to cover both high and low current density areas and provide a bright deposit. The electroplated chromium then gives the product the required colour and scratch resistance. Each industry will have its own specification on the thickness of the nickel and chromium deposit depending on the application. The automotive industry requires high level of corrosion performance on objects such as car bumpers as they are exposed to the atmosphere and environmental changes. Alternatively the interior door handles would not require the same level of corrosion protection but must provide good abrasion resistance and maintain their appearance.

The nickel and chromium electroplating process is very versatile and as a result many industries take advantage of this. A few examples of industries and their applications are listed here

- The automotive industry uses the process on car bumpers and interior trims
- The sanitation industry uses nickel and chromium on showers, taps and towel rails
- House interior manufacturers use the process on door handles, switches and other visible fittings

There are commercially available alternatives to nickel, such as white bronze, in applications where nickel was used as a topcoat for products such as costume jewellery (Simon 1994), this will be explained in more detail in chapter 2. At present there are no commercial alternatives for nickel in the application under chromium.

1.3 Research aim and objectives

The main aim of this research is:

"to find a commercial replacement for nickel as a suitable layer under decorative trivalent chromium surface for the electroplating industry"

This will enable electroplating companies to move away from the toxic chemicals used today and use a less harmful and more environmentally acceptable alternative.

The following objectives will be taken into consideration during the course of this study:

- Review current commercial plated deposits that have been formulated, and evaluate the deposits.
- Review current formulated deposits that have not been commercialised and evaluate the deposit.
- Investigate new potential formulations which may include adaptations of additives within an existing process.

While working towards the aim and objectives set out here, each proposed alternative will undergo evaluation to determine the following:

- The compatibility with trivalent chromium as opposed to hexavalent chromium.
- Its ability to fit within an existing plating line.
- The finished surface must show equivalent L*a*b* colour values, hardness, toughness and adherence characteristics.
- The corrosion protection must be at least equivalent to that of nickel and chromium.
- The chemicals used must not be more harmful or aggressive than the existing solutions used today, including the final deposit.
- Process control must not be more labour intensive than the existing nickel electrolyte, so not increase the process cost.
- The deposition rate must be similar to that of nickel.

- The cost of the process must not be more than the nickel process.

By adhering to the guidelines set out in this section any potential alternatives to the nickel deposit will be identified and robustly evaluated to fulfil the projects objectives.

1.4 Research approach

The main goal of this research is to produce a product that will be a commercially viable and robust alternative to the nickel deposit. The best approach to achieving this goal is to carry out an intensive literature review on the procedure of electroplating nickel and chromium, thus including the process control and also what alternatives have already been investigated and are available.

The next stage is to identify what techniques can be used to characterise the deposits, this will provide a structured template for each selected alternative including nickel to undergo an unbiased evaluation process. All aspects will be covered from the corrosion performance, the compatibility with chromium, to the general appearance of each deposit, while taking into consideration the cost and classification of each chemical process. Not all suggested alternatives will undergo the full evaluation; if simply the initial plating test identifies it as incompatible with chromium then further testing would be meaningless. It will be just as important to identify deposits that cannot replace nickel as well as the ones that can, by doing this a complete study will be represented.

The following stage will be to organise the results into a format that will be easily interpreted, this will identify which alternatives can be used as a replacement for nickel and in which application. This evaluation process will highlight the advantages and disadvantages of each alternative and from this a strong basis for a discussion will be formed. Once all the results are reported and the discussion for each alternative has been clearly noted, a reasonable, scientific conclusion will be made bringing the whole study together.

1.5 Contribution to knowledge

Today there is a wealth of knowledge in terms of the chemical hazards to both human health and the environment; as a result legislations are being set out to protect our future. This study will contribute to knowledge and understanding of alternative chemicals that can be used to safe guard our health and help preserve our environment, while being applicable to an application that is widely used in numerous industries. This research therefore will make the following contributions:

1. A critical review of the current situation in terms of the use of nickel and four of its soluble salts, including why alternative chemicals are being researched and the need for regulations on the use of these toxic chemicals, plus the impact it has on the electroplating industries.

2. A full characterisation of nickel and chromium will be carried out so a bench mark can be set up to assess potential alternatives, thus clearly identifying if nickel can be replaced in certain applications.

3. Provide awareness of limitations of both the nickel and potential alternatives to provide a foundation for further research and developments within this study.

4. Provide researchers with a comprehensive study and methodology to help them evaluate the advantages and disadvantages of any identified alternatives to the nickel deposit under chromium so they can make an informed decision to replace the nickel deposit in a commercial environment.

The overall outcome is to find an alternative to nickel deposit under chromium which will limit the impact of damage to our health and the environment while still providing a commercial process which is acceptable by industry productions.

1.6 Scope and limitations of research

While conducting literature reviews and research into the commercial applications of nickel and chromium electroplating it became apparent that there was no commercial alternative for this process. Alternatives to nickel were documented and commercially available but not in its application under chromium. The study started by identifying the most common alternative for nickel commercially used, this was known as white bronze. White bronze also known as speculum is formulated using cyanide which is also a toxic chemical. The literature identified numerous cyanide free formulations but with no commercial success due to the instability of the electrolytes. This gave the study a new direction of researching a cyanide free white

bronze but time constraints limited the progress made due to the focus of finding an alternative to nickel.

The white bronze process does not have its own additive system and so is used in conjunction with a bright copper deposit underneath, thus providing the required bright and levelled finish. Therefore commercially plated white bronze has a plated thickness of around 1µm, thus limiting the applications. The development of an additive system would be a project within itself and therefore beyond the scope of this research.

Since this project is investigating a commercial process it could arouse commercial interest and therefore requires a level of confidentiality. Company confidentiality can cover anything from a whole process or just certain chemicals used in their additives to enhance a process, thus making it difficult to find published work to back up claims.

1.7 Thesis outline

The thesis is broken down into eight chapters with a brief review of each chapter as follows:

Chapter One clearly outlines the aim and objectives to the study, the background to the research, the research approach and contribution to knowledge including the limitations and outline of the thesis.

Chapter Two presents the literature review of nickel and its soluble salts reclassified as toxic chemicals while also documenting the regulations and legislations in place for electroplating industries.

Chapter Three explains the electroplating process for both nickel and chromium in their existing applications and an explanation of how additives can improve the deposition process. This chapter also covers other aspects of plating such as alloy plating, including the applications.

Chapter Four explains the principles of metallic corrosion and the use of metallic coatings as a protective layer to control corrosion. A detailed explanation is given on how nickel and chromium coatings are used to control the corrosion path and increase the longevity of the deposits. Techniques used to accelerate and evaluate corrosion are also explained.

Chapter Five is the research methodology, where all the instrumental techniques used to characterise the electrodeposited coating including the plating sequence and conditions are explained. This chapter also explains why each technique was used, including the benefits and limitations in order to give a clear and concise comparison between deposits.

Chapter Six outlines the results in this study, providing information to characterise nickel and chromium deposits and also discusses alternative deposits that are feasible. The results will be discussed to assess which alternative deposit has the

potential to replace the nickel deposit in terms of the properties and characteristics identified in this study.

Chapter Seven concludes the whole study and presents key research outcomes. Here, the alternative to the nickel are highlighted and the applications that best suit the properties of the deposit are documented giving an overall conclusion to this research.

Chapter Eight will highlight recommendations for future work to either investigate a new approach or to continue with this study. As time restrictions are always present in research not all areas can be covered in the detail required, therefore this chapter provides an opportunity for the study to be continued if deemed feasible.

Summary

Chapter one has given an over view of this study including the background to the research, problem statement, research aim and objectives, research approach, contribution to knowledge, limitations to the research and outlined the structure of the thesis. The need to replace nickel deposition has passed through legislation and the proposal to find an alternative has been explored.

CHAPTER 2: LITERATURE REVIEW

Introduction

This chapter describes the health and environmental issues the electroplating industry faces when using both nickel and chromium electrolytes, it also documents the existing commercial alternatives for nickel including their applications whilst also investigating how the increasing cost of nickel has affected the electroplating industry over the last decade. Chapter 2 will clearly identify the foundation and understanding as to why the electroplating industry requires an alternative to nickel under chromium, by presenting a detailed literature review of today's issues and concerns.

2.1 Nickel and its salts used within the electroplating industry

Nickel is used in various applications in the electroplating industry, it has numerous properties which include, optimising the appearance of the plated component and providing improved corrosion protection. These properties make nickel a valuable metal to the electroplating industry.

2.1.1 Discovery of nickel

The Saxon miners found nickel arsenide and mistook it for copper oxide, which is also reddish in colour. They tried to extract the copper form what they thought was the copper oxide, as this was not possible they named it "Kupfernickel" meaning Devil's Copper or Old Nick's Copper (Greenwood 1997). Later in 1751 Axel

Fredrik Constedt in Sweden, isolated an impurity from a Swedish ore and identified it with kupfernickel. The identified metal was then given the new name "Nickel". It was another 50 years before J. B. Richter in 1804 produced a purer sample to determine more accurate physical properties of nickel.

2.1.2 Physical properties of nickel

Nickel is a lustrous silvery white metal; it is hard, ductile and can be sculpted, it is ferromagnetic and a conductor of heat and electricity. Nickel is the 24th element in order of natural abundance and the fifth most common element on earth with 6% in the earth's core and 0.0075% widely distributed in the earth's crust (Kasprzak 2003; Nickel-Institute 2003). Depending on geographical location, the abundance of nickel in soil is 5-500 parts per million and in natural river water it is approximately 0.3 parts per million (Nickel-Institute 2003). Nickel is also found in meteorites, weathering rocks and in the atmosphere from dust produced by volcanic emissions, the global input of nickel into the human environment is 330,000 metric tonnes per year with only 150,000 metric tonnes coming from natural sources; the remaining is from human impact by burning fossil fuel and industrial production to name a few examples (Kasprzak 2003).

2.1.3 Chemical properties of nickel

Nickel has the symbol Ni; it can be found in the periodic table among the transition metals, group 10, period 4, Table 2.1 summarises some of the properties of nickel. Nickel can be found naturally in five isotopic forms 58, 60, 61, 62 and 64. The most

common being 58 making up 67.8% of all nickel, the least common being 61 and 64 equally making up a total 2.4% of all nickel, the other isotopes 60 and 62 make up the remaining 29.8% (WHO 2005). Nickel has many oxidation states, the most common being 0 and +2, compounds containing +1 oxidation states are scarce and higher oxidation states +3 and +4 occur in certain complexes; however they are less stable than the lower oxidation states. Nickel is attacked by dilute acids such as hydrochloric and sulphuric in the presence of oxygen and is easily dissolved in nitric acid, although strong nitric acid can passivate the nickel. Sulphuric, hydrochloric and nitric acids dissolve nickel oxide to form the water soluble compounds nickel sulphate, nickel chloride and nickel nitrate respectively. Basic compounds such as nickel carbonate and nickel hydroxide also dissolve in acids to form salts.

Properties	
Atomic number	28
Atomic weight	58.9634
Number of protons/electrons	28
Number of neutrons	31
Electronic configuration	$[Ar]3d^8 4s^2$
Melting point ^oC	1455
Boiling point ^oC	2920
Density 20^oC/g cm^{-3}	8.908
Standard state 298 K	Solid
Colour	Lustrous, metallic, silvery tinge

Table 2.1. Properties of metallic nickel

2.2 Classification of nickel

In February 2007 there was the reclassification of the five nickel substances, the soluble nickel compounds (nickel sulphate, chloride, nitrate and carbonate) became classified as category 1 human carcinogens by inhalation (known to be carcinogenic to man) and category 2 reproductive toxicants (may cause harm to the unborn child) and chronic toxicant (T; R48-23). Nickel metal became classified as category 3 carcinogen (limited evidence of a carcinogenic effect) and chronic toxicity (T; R48/23). Table 2.2 illustrates the full classification list of metallic nickel and the four soluble nickel salts.

Health issues	**Nickel Metal**	**Nickel Sulphate**	**Nickel Chloride**	**Nickel Nitrate**	**Nickel Carbonate**
Acute Oral	None	Xn: R22	T: R25	Xn: R22	T: R25
Acute Inhalation	None	Xn: R20	T: R23	Xn: R20	T: R23
Skin Irritant	None	Xi: R38	Xi: R38	Xi: R38	Xi: R38
Eye Irritation	None	None	None	Xi: R36	Xi: R36
Skin sensitisation	R43**	R43*	R43*	R43*	R43
Respiratory sensitisation	None	R42	R42	R42	R42
Chronic Toxicity	T: R48/23	T: R48/23	T: R48/23	T: R48/23	T: R48/23
Reproductive Toxicity	None	Cat.2: R61	Cat.2: R61	Cat.2: R61	Cat.2: R61
Mutagenicity	None	Cat.3: R68	Cat.3: R68	Cat.3: R68	Cat.3: R68
Carcinogenicity	Cat 3:R40	Cat.1: R49	Cat.1: R49	Cat.1: R49	Cat.1: R49

* = 0.01% concentration limit (except for carbonate)
** = concentration limit based on release rate of 0.5µg Ni/cm^2/week

R20 Harmful by inhalation
R22 Harmful if swallowed
R23 Toxic by inhalation
R25 Toxic if swallowed
R36 Irritant to eyes
R38 Irritant to skin
R40 Limited evidence of a carcinogenic effect
R42 May cause sensitisation by inhalation
R43 May cause sensitisation by skin contact
R45 May cause cancer
R48/23 Toxic – danger of serious damage to health by prolonged exposure through inhalation
R49 May cause cancer by inhalation
R61 May cause harm to the unborn child
R68 Possible risk of irreversible effects
Xi Irritant
Xn Harmful
T Toxic

Table 2.2. Classification of metallic nickel and four soluble nickel salts (Nickel-Institute 2005).

2.3 Health and environmental impact of nickel

In 1996, an EU risk assessment was set up to investigate nickel and its compounds with regard to the effect it has on human health and environmental impact, an EU risk assessment evaluates and sets out controls for existing substances imported into the EU when volumes exceed 10 tonnes per year. The nickel substances in question need to be on the priority list for an EU risk assessment to start and a Member State volunteers to act as Rapporteur, in this case, it was the Danish Environmental Protection Agency (D-EPA). Five listed priority substances underwent risk assessment, these include nickel metal, nickel sulphate, nickel chloride, nickel nitrate and nickel carbonate.

2.3.1 Environmental issues

The EU risk assessment was used to set out the regulations on nickel and its salts, not only in Europe but also worldwide (ENIA 2005). An environmental risk assessment requires research into the safe level of nickel in the environment. The predicted no effect concentration (PNEC) suggests that less than or equal to the values set, there is a low probability that an unacceptable effect will occur, this value is compared to the predicted environmental concentration (PEC) which estimates the environmental concentration based on measured or calculated data. These two sets of data can be used to calculate a risk characterisation ratio (RCR) by dividing the PEC by the PNEC, if the result is >1 then a risk to the environment is assumed (ENIA).

The overall results of the risk assessment are as follows: (Rapporteur-Denmark 2008)

> *"**Conclusion 1** There is a need for further information and/or testing."*
>
> *"**Conclusion 2** There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already."*
>
> *"**Conclusion 3** There is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account."*

The conclusions were reached based on the following: (Rapporteur-Denmark 2008)

> *"**Conclusion 1** There is a need for additional testing to provide robust data for the derivation of the PNEC sediment."*
>
> *"**Conclusion 2** The risk assessment has shown that exposure of nickel at the regional scale results in no risk for most scenarios in the aquatic and terrestrial compartments. Additionally, no regional risk was shown for secondary poisoning."*
>
> *"**Conclusion 3** The risk assessment has shown that exposure of nickel at the regional scale causes potential risk to aquatic organisms in waters with high pH and low Dissolved Organic Carbon. Also, subsets of soils from Spain and the UK show potential risk. Several instances of risk to the aquatic and terrestrial compartments were observed for specific sites in the Local Scale risk characterization."*

There is data available for the nickel content in the environment but very little data on the bioavailability of nickel ions, it is the nickel ions that are absorbed by plants through the uptake of water from the soil and thus introducing nickel into the food chain. If this data was available, it would be more significant to help establish the health risks to living organisms rather than the total nickel content (ENIA 2005).

2.3.2 Health issues associated with nickel

Nickel is associated with numerous health issues that affect the electroplater and the general population, the health risks include nickel dermatitis, which can affect anyone and the risk of cancer, which is a concern for industries that handle the toxic nickel salts.

2.3.2.1 Nickel dermatitis

Nickel is a known allergen and causes allergic contact dermatitis (ACD). Numerous studies have shown that a higher percentage of women than men are suffering with ACD, the estimated figures vary slightly between published studies, but it is thought that around 5-10% of women and 0.5-1% of men suffer from ACD (Menne 1989; Kwangsukstith 1995). This difference is not fully understood but possible explanations are given although not proven, suggesting that women tend to become sensitised to nickel through contact with cheap jewellery, while men become sensitised through their exposure at work. Other reasons to suggest why there are gender differences were environmental, culture or biological makeup, such as the difference in hormone levels (Hemingway 1987; Kwangsukstith 1995; Gawkrodger 1996).

Nickel dermatitis also known in the electroplating industry as “nickel itch” occurs when nickel ions are absorbed into the body by combining with the protein components of the blood to form haptens, causing the immune system to react to the nickel ions by identifying them as foreign bodies and starting a counter attack, thus presenting as a rash (Leyendecker and Glaser 2000). The degree of sensitivity would

vary from person to person displaying anything from a red patch that would be slightly irritating (mild cases) to cracks in the skin and blisters that would cause acute pain (server cases). A person not allergic to nickel can become sensitised with continued contact and handling of nickel and its salts. A study by Hemingway in 1987 concluded that numerous factors increased the dissolution of nickel, 1) presence of oxygen, 2) friction, 3) applied pressure, 4) increasing contact time, 5) increasing the acidity (keeping within the pH range of natural sweat), thus increasing the risk of an allergic reaction.

The European community introduced an EU directive 94/27/EG with the technical standard EN 1819, EN 1811 and EN12472 to stop the use of nickel on parts that would be used for piercings on the body and restrict the use of nickel that would have prolonged contact with the skin. If nickel is to be used, it cannot release more than 0.5µg/cm^2/week over a period of two years, this also applies to any barrier layer used between nickel and the skin (Leyendecker and Glaser 2000).

Items that contain nickel are frequently used by the public on a daily basis; a good example of this is the United Kingdom's coinage. Table 2.3 identifies the coins that contain up to 25% nickel (BBC 2002; Royal-Mint 2008). A study was carried out examining the release of nickel from coins because of its allergenic properties (Linden 2001). The results showed that the surface of the cupro-nickel coins released 2 µg of nickel after 2 minutes of contact with artificial sweat, thus concluding that handling coins could cause an allergic reaction in people who are sensitive to nickel. Other items of everyday use that contained nickel were belt buckles, buttons on clothing and costume jewellery, the nickel was introduced as a cheap alternative to

silver due to its properties of a good barrier layer to the underlying copper and being more cost effective. In 2001 strict conditions were enforced in Europe concerning the use of nickel on consumer goods and its use was widely restricted (Bronder 2010).

Coin	Composition
5 pence coin	Cupro-Nickel = 75% copper + 25% nickel
10 pence coin	Cupro-Nickel = 75% copper + 25% nickel
20 pence coin	Cupro-Nickel = 84% copper + 16% nickel
50 pence coin	Cupro-Nickel = 75% copper + 25% nickel
£1 coin	Nickel-Brass = 70% copper + 5.5% nickel + 24.5% zinc
£2 coin outer section	Nickel-Brass = 76% copper + 4% nickel + 20% zinc
£2 coin inner section	Cupro-Nickel = 75% copper + 25% nickel
£5 Coin	Cupro-Nickel = 75% copper + 25% nickel (collectors versions have been struck in precious metals)

Table 2.3. Composition of coins made by the British Royal Mint (Royal-Mint 2008).

There are a small number of people who are known to be "hyper-sensitive" to nickel, this is when a very small amount of nickel such as that found in curtain types of stainless steel will start an allergic reaction (Haudrechy 1993). The study by Haudrechy showed that out of 50 people known to be allergic to nickel, 7 of them showed a reaction to resulphurised stainless steel (AISI 303), none of the 50 people showed a reaction to low sulphur containing stainless steels (AISI 304, 316 and 430). It was suggested that the low sulphur containing stainless steel has a chromium rich passive film which provides corrosion protection (even in acidic conditions of pH 4.5, similar to sweat) stopping the release of nickel which is also said to be tightly bound (Cerveny 2002). The resulphurised stainless steel found that the manganese sulphide dissolved in acidic conditions the same as nickel, thus allowing nickel to be released.

There have been numerous studies on how and why people become sensitised to nickel, one study carried out in Finland during 1991-1997 reported 2543 cases during the 7 year period of occupational ACD caused by metals, of which 176 cases were caused by nickel (Kanerva 2000). In Europe, nickel is the most common cause of ACD, thought to be because of cheap jewellery and the use of nickel salts in industries such as electronics, storage batteries, electroplating and ceramics. A study by Kwangsukstith in 1995 looked at the effect of age and gender on ACD and found there were higher incidences in adults than children. Further studies were required before a full conclusion could be made on the effects of age groups as adults were more likely to have contact with nickel (Kwangsukstith 1995).

The electroplating industry has a responsibility for the health and safety of its employees and therefore action must be taken to follow the COSHH (Control Of Substances Hazardous to Health) regulations 2002, by controlling the risk of skin exposure to nickel within a work place to prevent sensitisation. COSHH requires that skin exposure to nickel and its salts are prevented or adequately controlled at work, if prevention is not possible then the use of personnel protective equipment (PPE) is required; this would include hand gloves, eye protection and by wearing overalls. The Health and Safety Executive (HSE) states that the role of PPE should only be used as a last resort for removing any risk to health; all other measures must be carried out first. This is a way of being able to use nickel and its salts but still prevents skin contact and so limits the risk of employees becoming sensitised (HSE 2005).

2.3.2.2 Nickel as a carcinogen

There have been studies carried out on people who work within the nickel refining industry to evaluate the possible link between cancer and the exposure levels of nickel. A study published in 1997 investigates the health of people who work in the electrolytic nickel refining industry when exposed to soluble nickel compounds (Kiilunen 1997). This study was carried out at Outokumpu Harjavalta electrolytic nickel refinery in Finland. Thirty four workers represented all the main tasks within the plant and provided samples, including micronucleus analysis (one year after the study was complete), air quality whilst working, regular urine samples and also blood samples before and after the study. Further data was also provided for nickel concentrations of the air in the tank houses and also the breathing zone of the workers dating back to 1966. This extra data available is unusual and helps give a better understanding of the nickel exposure levels over many years and not just for the period of study. It is important to remember that this study only looks at soluble nickel compounds and so must not be confused with results from studies using insoluble nickel compounds.

The historical data shows the exposure levels of nickel were between 230-800µg/m^3 during 1966-1988 which were below the occupational exposure limit of 1mg/m^3 set in Finland. There were three workers reported to have nasal cancers who finished working at Outokumpu Harjavalta during 1977-1983, the company did provide masks but their use was not enforced and so rarely used. A decrease in nickel exposure levels after 1988 was reported to be 112-484µg/m^3, this was not due to a decrease in nickel exposure, but the fact that the samples were more representative of true nickel exposure to the worker, as results combined the use of a mask and not

just in the general atmosphere. From this information it is suggested that the use of a mask decreased the exposure to nickel although the study does not confirm this as air samples were only taken from inside the mask and not the surrounding atmosphere.

There has been a suggested correlation between airborne nickel concentrations and urinary nickel referenced by Kiilunen. The study from Outokumpu Hrjavalta indicated that airborne nickel could only account for 10% of urinary nickel, suggesting that nickel ions are absorbed by other routes. This theory was proven by the use of gloves, as nickel concentrations decreased in the urine when gloves were worn, indicating that the nickel concentration in urine can give a total uptake of nickel but unable to identify by which route. The study also concluded that concentrations of nickel were higher in electrolysis workers than the general public, indicating that nickel is being absorbed into the body whilst at work.

There is suggested evidence that nickel ions accumulate in the body, after a period of 2-4 weeks without nickel exposure the concentration of nickel in urine increases but no increase was seen in the blood. The results imply that nickel ions have an accumulative effect, but there is another possibility not mentioned in the study, a paper by Cleveland in 2002 suggested that nickel ions could move slowly through the body to the kidneys and be released into the urine, this would take a number of weeks for the body to process the nickel ions (Cleveland 2007). Other reports do indicate that nickel ions are removed by the kidneys over a period of time but there is very little reported evidence of transported nickel ions through the body by skin absorption (Cleveland 2007).

A review paper titled “Nickel Carcinogenesis” reports studies carried out on the link between nickel and a variety of pathologic effects (Kasprzak 2003). It highlights that the exact mechanism of nickel induced carcinogenesis is unknown but has been the subject of investigation in a number of studies (Oller 2002; Zoroddu 2002). The International Committee on nickel carcinogenesis in humans in 1990 suggested that respiratory cancer risks were related to exposure of nickel concentrations of above 1mg/m^3 and in less soluble nickel, concentrations of above 10mg/m^3 were considered a risk (IARC 1990). Other health problems mentioned included lung fibrosis, asthma, cardiovascular and kidney diseases (Bright 1997; Leikauf 2002). Great Britain declared that cancer among some nickel refinery workers was an industrial disease after a total of 129 reported cases by 1949. In a Welsh refinery nasal cancers are reported as far back as 1933, followed by 17 nasal and 19 lung cancers a few years later. Since this discovery studies on humans and on animals have confirmed this link. It was believed that only water insoluble nickel compounds were the cause, but more recent studies have found that soluble nickel compounds have a carcinogenic effect on the respiratory system and it can be dose related (Grimsrud 2003).

The animal studies indicated that insoluble nickel compounds were the most fatal carcinogen when compared to soluble compounds. Inhalation studies showed that rats exposed to nickel compounds such as tetracarbonylnickel and nickel subsulfide induced lung cancer and so did feinstein dust (dust produced in nickel ore processing containing Ni_3S_2). It reports no cancers were found in the control rats, but it is unclear if the control rats were exposed to nickel free dust. The control rats may not have been exposed to any dust and therefore concluding nickel to be a carcinogen

would be inappropriate due to the knowledge that particles of any description in the lungs can be harmful, an example of this is bakers lung, fine flour particles become airborne during the baking process and is inhaled by the baker causing respiratory problems (Droste 2003).

A review of previous studies into the carcinogenic effect of nickel, is important to remember that there is a limited amount of data published and so the full understanding of the results may be restricting and to some degree misleading. An assessment carried out by Oller in 2002 found that soluble nickel compounds do not cause cancer but at high concentrations they can cause chronic respiratory toxicity and enhance the tumour response elicited by inhalation of carcinogens such as cigarette smoke or insoluble nickel salts (Oller 2002). The problem with epidemiologic studies determining whether soluble nickel compounds have a causal or enhancing effect is the lack of full data available. Ideal conditions and required data necessary for a comprehensive epidemiologic study to produce an accurate conclusion would be, 1) full analysis of exposure limits, 2) isolation of soluble or insoluble nickel compounds, 3) no other contact with known or suspected carcinogenic substances like cigarette smoke, 4) health of the individual including any family history of cancers, 5) controls, where an individual has no contact with nickel in the work place or any other known or suspected carcinogenic substances. Lung cancer is associated with the inhalation of nickel salts, it is also associated with smoking and with a large portion of the population being smokers (1 in 4 people (National-Statistics 2006)), it is easy to see the difficulties in fulfilling the ideal requirements and isolate other carcinogens to identify if nickel salts are a cause of cancer.

If it is accepted that insoluble nickel compounds are a carcinogen and soluble nickel compounds can increase the risk of cancer, then information would be needed to see if they are also dose related. From the figures quoted earlier by the International Committee on nickel carcinogenesis in humans it is suggested that there is at least a level where a person would be at risk, but whether the increase in dose would increase the risk was not mentioned. A study by Grimsrud (Grimsrud 2003) identified a dose related effect from nickel exposure, which was easy to identify for soluble nickel compounds with little difference between nickel chloride and nickel sulphate. The recognised pattern was also adjusted to take into account smokers and potential occupational confounders and still found it to conform. The findings showed increased risk by the length of total employment, increased duration of work and the standardised incidence ratio increased with cumulative exposure to both total nickel and water soluble nickel.

2.3.2.3 Nickel ingestion into the body

Nickel concentrations in our foods generally range from 0.01-6 mg/kg. Seeds, nuts, and beans contain levels of 1-6 mg/kg of nickel, while cacao (raw material for making chocolate) has higher levels of 8-12 mg/kg of nickel (WHO 2005). Food and water is the most common route of nickel exposure to a person who does not smoke or work within the nickel industry, United Kingdom Total Diet Study in 1981 claimed that food contributed 0.22-0.23 mg/day of nickel intake per person, but more recent studies claim this figure is high and report less than 0.2 mg/day intake of nickel per person from food (WHO 2005).

The UK/European limit for nickel in drinking water is 40µg/l, up to 20µg/l can be introduced by the water supplier and another 20 µg/l allowed from an outside source (Seven-Trent 2005). Recently the World Health Organization (WHO) has raised the total level to 70µg/l allowing the outside source to increase to 50µg/l (WHO 2005). Nickel is introduced into the water supply from an outside source by leaching; this occurs due to the dissolution of nickel from the nickel/chromium plated taps. Chromium is known to have poor throwing power (distance chromium can cover in the low current density area) down the bore of a tap compared to electroplated nickel; therefore water being held in the tap is in contact with the nickel. Work has been carried out to see how much nickel is dissolved when mains water is left static in the tap for a period of time (Private Communication). It was concluded that after four hours the previous recommended limit of 40µg/l was reached, and after eight hours the new limit of 70µg/l was exceeded. Running water through the tap was also tested and found not to contain high levels of nickel, and therefore neither limit was reached. There are other outside sources that can introduce nickel to drinking water, these include stainless steel pipes (thought to introduce around 6 µg/l of nickel when pipes are new) nickel plated elements in kettles can introduce 100-400 µg/l of nickel and in extreme cases values over 1000 µg/l have been reported (BBC 2003; WHO 2005).

2.4 Impact of increasing cost of nickel to industries

A report published in Business Wire highlighted the stainless steel industry is still the main consumer for nickel by dominating 64% of global consumption, China and India's demand for stainless steel will continue playing a major role in the growth of

the global nickel industry (Wood 2008). The automotive and aerospace industries in countries such as US, Germany and the UK will also require nickel, maintaining an overall high demand for the metal. Figure 2.1 shows the cost of nickel over a period of seven years, although the price has dropped around US$12/pound from the peak in 2007, the price in 2008 was still US$10/pound, thus still being more expensive than in 2001. There are still no signs that the price of nickel is coming down as mining costs continue to increase due to mining strikes and equipment failures plus the increasing technological challenges of extracting the nickel keeps pushing the cost of nickel up (BBC 2006; Hotter 2006).

Figure 2.1. Price of nickel over a period of 7 years from 2001 – 2008.

The worlds nickel resources are found in two types or ore, laterite and sulphite. The laterite ore makes up 73% of the worlds nickel resource, while the more traditionally processed ore, sulphite makes up only 27%. Research has developed new capabilities

of processing the laterite ore which involves leaching technology, as with all processes there are advantages and disadvantages, these are summarised as follows:

> *<u>Advantages</u> of the leaching technology include the capability to process a mix of the ores and the excess power generated for the sulphur to produce the acid can be sold back to the local grid.*
>
> *<u>Disadvantages</u> with this process include the high capital cost which is estimated to run into billions of US$, more complicated process which has maintenance issues and a high consumption rate of acid.*

This new capability is estimated to introduce around 800kt of nickel by 2014 as primary nickel production is forecasted to grow 7% year-on-year between 2010 and 2014 (Jahangir 2010).

The increasing cost of nickel has encouraged design engineers and purchasing managers to discuss alternatives to 300-series stainless steel which contain 10% nickel, the alternatives include the ferric grades in the 400-series containing very little to no nickel and the lower nickel 200-series stainless steel containing <2% nickel (Stundza 2007). In 2004 the 300-series stainless steel accounted for 87% of China's total stainless steel output, over the next five to ten years it was predicted that this would reduce to 60% as the use of 200- and 400-series stainless steel would increase (Metal-Weekly 2004). The electroplating industry consumes around 8-9% of the industrial nickel consumption, this has led companies to invest in research to

find alternatives to nickel as the cost continues to increase (Morgan 1994; LME 2010).

2.5 Current alternative for electrodeposited nickel

The need to seek an alternative replacement for nickel in spite of its utility in the plating industry spanning over centuries, is a result of the health and safety issues concerning its use and its recent classification as a suspected carcinogen. This has been clearly detailed in section 2.2 with the implications associated to our health and environment in section 2.3. These are impending legislations prohibiting the use of nickel, therefore ongoing research to seek an alternative and suitable replacement is continuing. Replacements for nickel are available but, only for a limited number of applications, different approaches have been made in finding an alternative to electroplated nickel. One approach is to eliminate nickel completely, while the second approach is to reduce the nickel exposure. This study is in favour of eliminating nickel and its soluble salts completely, thus providing a safe alternative for both the electroplater and consumer.

2.5.1 Copper-tin alloys as an alternative to electroplated nickel

The use of bronze plating was first published in 1842 by Ruolz, making bronze plating over 150 years old (Brenner 1963). Copper-tin alloys known as bronze can vary in composition to change the properties of the alloy, for example, an alloy containing more copper will be yellow in colour, while more tin in the alloy will provide a silver colour. White bronze is an alloy composed of copper, tin and in some formulations zinc, the composition can vary but are typically found to be

between 50-55% Cu, 30-50% Sn and 0-15% Zn (Leyendecker and Glaser 2000). The white bronze alloy is reported to have a better corrosion resistance when compared to nickel, the higher level of tin provides a good resistance to tarnishing and artificial sweat, thus making it a ideal alternative to nickel in applications such as cheap jewellery, clothing buttons and fasteners where nickel dermatitis is eliminated but without compromise to the wear resistance (Simon 1994; Leyendecker and Glaser 2000; Brooman 2001). Alloy plating is explained in more detail in chapter 3.10

One disadvantage of white bronze is that the formulation contains cyanide; there are numerous patents and papers published identifying cyanide free electrolytes for brass and bronze deposits but they are not commercialised due to varying issues (Johannsen 2000; Pewnim 2011). The cyanide free formulations based on pyrophosphates or oxalates produce a spongy deposit with a dull appearance and an uneven colour tone (Kaneko 2002). Unlike the pyrophosphate and oxalate electrolytes that operate around pH 7-10, 25-50^{o}C with a cathode current density of 0.05-10A/dm^{2}, electrolytes based on alkylsulfonic acids produce a better deposit due to a faster plating rate. The alkylsulfonic acid electrolytes can operate at room temperatures and at a pH <1 allowing divalent tin to reduce to metallic tin more easily. With all the formulations the introduction of divalent copper into the electrolyte causes difficulties in controlling the chemical and physical parameters to obtain an acceptable alloy deposit. The potential difference between the copper and tin leads to higher rates of oxidation of the divalent tin to tetravalent tin, tetravalent tin cannot be electrodeposited, thus resulting in a sludge formation in the electrolyte (Zschintzsch 2006; Hovestad 2008), equation 2.1 demonstrates the reaction. The Cu-Sn alloy deposit changes and becomes copper rich due to the low levels of

divalent tin and so the electrolyte becomes unstable, making the process unsuitable for commercial production.

$$Sn^{2+} + 2Cu^{2+} \rightarrow Sn^{4+} + 2Cu^{+} \qquad (2.1)$$

Many cyanide free formulations have been published with claims to either improve stability of the electrolyte or the appearance of the alloy deposit. A study by Zschintzsch et al in 2006 filed a patent using alkylsulfonic acid electrolyte, which included stabilisers or complexing agents such as sodium gluconate and oxidation inhibitors such as pyrocatechol to slow down the oxidation of divalent tin (Zschintzsch 2006). To improve the Cu-Sn alloy deposit the use of brighteners (carbonyl compounds) and wetting agents (polyethylene glycols) were reported. Research carried out by Carlos et al on the effect of tartrate on a cyanide free Cu-Sn electrolyte based on alkylsulfonic acids claimed to identify no change in the electrochemical efficiency values over a period of four weeks, the electrolyte containing no tartrate showed gradual decrease in the electrochemical efficiency over the same period of time. The conclusion is that the tartrate extends the life of the electrolyte, but from a commercial aspect an electrolyte must be stable for a much longer period (Carlos, Bidoia et al. 2002). The use of thiourea has also been published claiming to increase the life of the electrolyte, the patent states that there is no complexing agent used and therefore poses no effluent problems due to the thiourea working as an oxidising inhibitor (Muramatsu 2002). The electrolyte still presents the same issues of stability, this is thought to be because the thiourea is a known complexing agent and will complex copper +1 ions, the complex has four ligands with a stability constant of 15.4 (Bjerrum 1957). With this in mind any

copper +1 ions in the electrolyte have the potential to complex with the thiourea, expanding the life of the electrolyte but causing effluent problems on disposal.

The application for white bronze as a topcoat only requires a few micrometers of deposit, the copper deposit underneath must provide the levelling and brightness required due to the fact that white bronze does not have its own additive system. The white bronze deposit tends to be porous and should not be plated directly onto steel due to the steel being more anodic (Brooman 2001).

There have been numerous publications identifying white bronze as an alternative to nickel, for instance, research published by Simon in 1994 states that white bronze has better corrosion resistance than nickel and also the ability to withstand artificial sweat (Simon 1994). Another study by Leyendecker et al in 2000 identifies the white bronze to be more corrosion resistant than nickel on a brass substrate when tested in a sulphur containing atmosphere (Leyendecker and Glaser 2000).

White bronze was also shown to be only slightly softer than nickel with hardness figures of 550HV and 600HV respectively. Nickel was identified to have better abrasion resistance than white bronze with a weight loss of 18mg/1000 revolutions compared to 50mg/1000 revolutions respectively (Leyendecker and Glaser 2000). White bronze is clearly documented as a commercial product used as a top coat but not as an intermediate layer under chromium, this research will therefore focus on the use of white bronze as an intermediate layer under chromium with a view to replace nickel. The results would be presented in chapter 6.

2.5.2 Palladium as an alternative to electroplated nickel

Palladium is by far the most expensive replacement for nickel, its applications would best suit the replacement where nickel was used as a barrier layer to stop the diffusion of the underlying copper into the top layer of gold. Applications such as eyeglass frames use this process to keep the cost of gold down since a thinner layer can be plated. The diffusion properties of palladium are equal to those of nickel but it does not have its own levelling or brightener system, thus limiting the application. To achieve a bright finish, the deposit is required to be 99.9% pure and can only be plated up to a thickness of 10µm giving a hardness value of 250 VHN, which is softer than bright nickel reported to be 300 VHN (Simon 1994).

2.5.3 Gold as an alternative to electroplated nickel

A gold alloy containing 1.4 to 1.7% iron will give the deposit in the range of 23.5 carats with a hardness of 220VHN and is tarnish resistant, this alloy would be a typical alternative for the gold/nickel alloy used as a decorative finish, but would not be a substitute for bight nickel. The gold/iron deposit is softer than the nickel deposit and the appearance would be of a yellow colour. Other nickel free gold alloys are listed in Table 2.4, these deposits will vary in appearance and will have different properties but are unlikely to be an acceptable alternative due to the colour and softness of the deposit compared to the bright nickel. Therefore, the gold alternative would not meet the requirements for the applications outlined in this study .

Nickel free gold alloys
Gold/tin
Gold/silver
Gold/copper/silver
Gold/palladium
Gold/copper/palladium
Gold/cobalt

Table 2.4. Nickel free gold alloys.

2.5.4 Tin as an alternative to electroplated nickel

Tin can be used in the clothing and jewellery industry to replace nickel; the deposit can be either dull or bright, thus producing a variety of different finishes. A bright tin deposit is not sensitive to finger printing and offers good wear resistance, thus could be an ideal finishing for items that are handled frequently (IMF 2011). Tin is also alloyed with other metals; section 2.5.1 details the alloy of copper and tin. Depending on the application, the tin deposit can be plated to the required thickness, typically for clothing fastenings and jewellery. It is confirmed that 5-7.5µm of tin is required to stop discolouration from the underlying substrate (Simon 1994; Cerveny 2002).

Tin offers good corrosion protection to steel when plated to a minimum of 50µm, but high strength steels are prone to hydrogen embrittlement and sometimes heat treatment is required to eliminate brittleness (IMF 2011). Tin is a softer metal compared to nickel so by using tin in an alloy the hardness of a deposit can be improved, this can been seen with the use of a Cu-Sn alloy deposit.

Tin is used in the electronics industry to replace lead, but this has been problematic due to the formation of "tin whiskers", this is when the electroplated tin on standing continues to form microscopically small needles of tin oxide, as they grow they can then come into contact with other components in the circuit causing current leakage and short circuits has been recognised (Dittes 2003). The addition of copper, can significantly reduce the whisker growth, thus producing an alternative to lead in the electronic industry (Dittes 2003). A deposit of tin/manganese is published as an alternative to tin/copper but found to grow tin whiskers much faster. Since tin whiskers are not an issue with the application outlined in this study, this alloy has the potential to replace nickel deposit under chromium.

2.6 Chromium used in the electroplating industry

2.6.1 Discovery of Chromium

The name chromium is derived from the word *chroma* meaning colour due to the variety of colours found in the compound discovered in 1797 by a French man named Louis Vauquelin. The oxide of a new chromium element was found by method of charcoal reduction in a mineral called Siberian red lead, known today as crocoite ($PbCrO_4$) (Greenwood 1997). It was in the late 1920's when chromium plating was discovered and found to offer a bright finish that did not tarnish and was almost indestructible. The fast development due to high demand led to the chromium deposit not being fully studied, therefore it was thirty years later when research discovered that chromium not only improved the appearance and abrasion resistance but also contributed to improving corrosion resistance (Draper 1961).

2.6.2 Physical properties of chromium

Chromium is a solid silver-grey metal with a density of 7.18g/cm^3 and has a melting point of 1907^oC, it can be highly polished and will not tarnish in air. It is the 21st most abundant element in the earth's crust with an average concentration of 100ppm (Emsley 2001). Chromium is found in the environment due to erosion of rocks and volcanic eruptions, the concentration of chromium in the soil ranges from 1-3000mg/kg, its concentration range in the sea is 5-800µg/L and 26-52µg/L in lakes/rivers (Kotas 2000). Chromium is mined as chromite ($FeCr_2O_4$), there are copious amounts of chromite but it is concentrated in South Africa and Kazakhstan which stores about 40% of the ores concentration. Other substantial producers of chromium are in India, Russia and Turkey (National-Research-Council-(US) 1974). Chromium is unstable in oxygen and as a result forms an oxide layer which is impermeable to oxygen, thus protecting the metal below. Chromium is antiferromagnetic at room temperature and above 38^oC it transforms into a paramagnetic state (Fawcett 1988).

2.6.3 Chemical properties of chromium

Chromium has the symbol Cr and can be found in the periodic table among the transition metals, group 6, period 4. Naturally occurring chromium is made up of three isotopes, 52, 53 and 54, the most abundant being 52. There is a wide range of available oxidation states, where +3 and +6 are the most common, chromium with an oxidation state of +6 is a strong oxidant, while chromium with a +3 oxidation state is the most stable. Table 2.5 shows some properties of chromium.

Properties	
Atomic number	24
Atomic weight	51.9961
Number of protons/electrons	24
Number of neutrons	28
Electronic configuration	$[Ar]3d^5 4s^1$
Melting point ^oC	1907
Boiling point ^oC	2690
Density 20^oC/g cm^{-3}	7.19
Standard state 298 K	Solid
Colour	Grey

Table 2.5. Properties of chromium

2.7 Classification of chromium compounds used in electroplating

Chromium trioxide is the chemical used to electroplate chromium form the hexavalent oxidation state, it is a human carcinogen and toxic if swallowed, inhalation may cause serious lung damage and it can cause burns or ulcers when in contact with the skin. Table 2.6 lists the full risk phase for chromium trioxide (University-of-Oxford 2007).

Risk Phase for chromium trioxide	Explanation of risk phase
R9	Explosive when mixed with combustible material
R24	Toxic in contact with skin
R25	Toxic if swallowed
R26	Very toxic by inhalation
R42	May cause sensitisation by inhalation
R43	May cause sensitisation by skin contact
R45	May cause cancer
R46	May cause heritable genetic damage
R50	Very toxic to aquatic organisms
R53	May cause long term adverse effects in the environment
R62	Risk of impaired fertility

Table 2.6. Risk phases and explanation for chromium trioxide used in chromium electroplating.

Chromium sulphate is used in electroplating chromium from the trivalent oxidation state, the classification is harmful if swallowed and an irritant. Table 2.7 give the risk phases for chromium sulphate (University-of-Oxford 2005).

Risk Phase for chromium sulphate	Explanation of risk phase
R22	Harmful if swallowed
R36	Irritating to eyes
R37	Irritating to respiratory system
R38	Irritating to skin

Table 2.7. Risk phases and explanation for chromium sulphate used in chromium electroplating.

The different classifications between the two chromium compounds clearly shows that trivalent chromium is less harmful to both living organisms and the environment; therefore by replacing hexavalent chromium with trivalent chromium the associated health risks to the electroplater are reduced.

2.8 Health and environmental impact of chromium and precautionary measures

Chromium plating is a valued decorative finish used in the electroplating industry, offering both corrosion protection and improved appearance to the substrate. With growing concerns on the impact that chemicals have on our health and the environment there are always researchers striving to find more acceptable alternatives. Precautions are taken by industries to limit and minimise the release of toxic chemicals, extraction process is used to remove gases and fine particle spray from the working area, while fume scrubbers are used to stop the extracted contaminated air reaching the atmosphere. Effluent plants are used to treat waste water before it is introduced back into the main water supple or recycled within the facility. The above are examples of good working practice but malfunction of equipment or human error can still occur resulting in the hazardous chemical reaching the environment. An alternative less harmful chemical therefore would be preferred if it reduce the risk to our health and environment.

Hexavalent chromium is found naturally in the environment, but industries such as electroplating, textile and leather manufacturing have the potential to introduce hexavalent chromium into the water system, thus having a detrimental impact on the aquatic life. Waste disposal and coal processing industries could introduce hexavalent chromium into the soil and atmosphere respectively, thus being problematic to vegetation and affecting the food chain. There are legislations in place to control the use of hexavalent chromium and other toxic chemicals. The Control of Major Accident Hazards (COMAH) regulations states the following: (HSE 2010)

> "*Take all necessary measures to prevent major accidents involving dangerous substances. Limit the consequences to people and the environment of any major accidents which do occur."*

Companies that handle more than 5 tonnes of chromium trioxide will need to register as a lower tier and over 20 tonnes as a top tier COMAH site (Gardner 2006). The End of Life Vehicle Directive (ELV directive) is in place to protect the environment when the vehicle becomes scrapped or recycled, the use of hexavalent chromium is banned on vehicles made for use in the European market (Environmental-Agency 2011).

Trivalent chromium enters the environment both naturally and by human activity. Industries such as electroplating, metal polishing and dye/pigment manufacturers used trivalent chromium, therefore have the potential to release it into the environment. As the chemical is less toxic than hexavalent chromium the consequences are not as severe. Vegetation require a level of trivalent chromium and can control the uptake, problems arise if the soil becomes too acid then it is possible for the vegetation to increase the uptake having a detrimental effect. Trivalent chromium is required in our diets to help maintain our metabolism, but at increased levels it can become detrimental to the body. If trivalent chromium accumulates in fish it can harm the gills causing respiratory problems, thus in turn disrupting the food chain if large colonies are affected.

Hexavalent chromium has serious effects on human health, it is an allergen that can cause a rash in people who are allergic and if inhaled can cause nose bleeds and ulcers. More serious health risks are respiratory problems, weakened immune system, liver and kidney damage, heritable genetic damage and risk to fertility, lung cancer and even death. Trivalent chromium is a nutrient for humans, low levels can disrupt the metabolism, cause heart conditions and diabetes, high levels can cause skin rashes and have a detrimental effect on health (Guffie 1986; Legg 1996; Khan 2005; Shuker 2005).

Trivalent chromium is more tolerated within the environment and is essential in low levels to some organisms, thus making it less toxic than hexavalent chromium, therefore trivalent chromium is more acceptable to use than hexavalent chromium. This study will concentrated on trivalent chromium electrolytes to deposit the chromium onto the alternative coating used to replace the nickel deposit. A study by Lansdell compares the surface activity and corrosion resistance of decorative electrodeposits from hexavalent and trivalent chromium electrolytes (Lansdell 2001).

Summary

This chapter has provided a detailed literature review on both nickel and chromium outlining the importance they have on our day to day life and also identifying the dangers of these useful but hazardous chemicals. Chapter 2 has highlighted some existing alternatives to nickel but no publications can be found for their application as an alternative to nickel under chromium.

CHAPTER 3: THEORY OF METALLIC DEPOSITION

Introduction

This chapter describes the principles of electroplating and the variables used to control a process. There are many applications that use nickel and chromium and some will be detailed in this chapter. A number of chemicals used to produce nickel and chromium electrolytes are categorised as toxic, thus having a negative effect on both the environment and our health. This chapter details the implications of exposure to such toxic chemicals, and recommends safer commercial alternatives to use.

3.1 General principles of the electrochemical series

Metal ions in solution behave differently under equilibrium compared to when an electric current is applied. The electrochemical series lists elements in order of their standard electrode potentials so the elements that ionise with ease can be identified with relation to the other elements. Table 3.1 shows the order for some of the common metals used in electroplating; the voltage is calculated by using the Nernst equation as explained in section 3.7.

When looking at the reactivity series, Table 3.1, the more electropositive the metal is the less reactive it is, as metals oxidise and loose electrons, they form cations. Take iron for example, metallic iron is known for reacting with the atmosphere and rusting, to form iron (III) oxide. When compared to gold reacting with the atmosphere, it is a much slower reaction because gold is more electropositive than

iron and so remains in its metallic state for a longer period of time, making gold a good metal for jewellery.

$CrO_2 + 2H_2O + 3e^-$	$\leftrightarrow$	$Cr + 4OH^-$	-1.200 V
$Mn^{2+} + 2e^-$	$\leftrightarrow$	Mn	-1.029 V
$Zn^{2+} + 2e^-$	$\leftrightarrow$	Zn	-0.763 V
$Cr^{3+} + 3e^-$	$\leftrightarrow$	Cr	-0.740 V
$Fe^{2+} + 2e^-$	$\leftrightarrow$	Fe	-0.409 V
$Cd^{2+} + 2e^-$	$\leftrightarrow$	Cd	-0.403 V
$Co^{2+} + 2e^-$	$\leftrightarrow$	Co	-0.280 V
$Ni^{2+} + 2e^-$	$\leftrightarrow$	Ni	-0.230 V
$Sn^{2+} + 2e^-$	$\leftrightarrow$	Sn	-0.136 V
$Fe^{3+} + 3e^-$	$\leftrightarrow$	Fe	-0.036 V
$2H^+ + 2e^-$	$\leftrightarrow$	H_2	0.000 V
$Sn^{4+} + 2e^-$	$\leftrightarrow$	Sn^{+2}	0.150 V
$Cu^{2+} + 2e^-$	$\leftrightarrow$	Cu	0.340 V
$Cu^+ + e^-$	$\leftrightarrow$	Cu	0.522 V
$Ag^+ + e^-$	$\leftrightarrow$	Ag	0.800 V
$Au^{3+} + 3e^-$	$\leftrightarrow$	Au	1.420 V
$Au^+ + e^-$	$\leftrightarrow$	Au	1.680 V

Table 3.1. The electrochemical series (Weast 1980)

To demonstrate the reaction of how a less electropositive metal, iron for example, is displaced by a more electropositive metal in its ionic form, copper sulphate for example, can be explained when a metallic iron bar is immersed into copper sulphate solution. Copper ions will be reduced to copper metal on the iron bar as the iron metal is oxidised to iron ions forming ferrous sulphate as expressed in equation 3.1. The ions in solution will diffuse from a region of high concentration to a region of

lower concentration (known as the concentration gradient explained in section 3.3.5) so there is a constant supply of copper ions at the iron metal bar.

$$CuSO_{4(aq)} + Fe_{(s)} \rightarrow Cu_{(s)} + FeSO_{4(aq)} \qquad (3.1)$$

This principle is the same when current is applied to a solution containing more than one metal ion. The more electropositive metal will plate preferentially to the less electropositive metal, only when the reduction potentials are of similar value will the metals deposit together known as alloy plating (a full explanation of alloy plating can be found in section 3.10). The standard electrode potentials are only an indication of which metal will plate preferentially, it does not take into account polarisation effects that make the metals more electronegative and complexing agents which make the metal less electropositive. Further explanation of the metallic behaviour is given in section 3.10.3.

The electrochemical series does not explain how metals that are more electronegative than hydrogen still plate preferentially. In practice the activation energy required for hydrogen atoms to form hydrogen gas is higher than the activation energy for crystallisation of more electronegative metals, thus allowing metals such as nickel and zinc to be deposited. The activation energy of hydrogen can be affected by the substrate metal acting as a catalyst; an example of this is when high carbon steel substrate is used in an alkali zinc solution. The carbon will act as a catalyst for hydrogen evolution, the production of hydrogen gas will be the preferred reaction. Once zinc is deposited on the substrate it becomes difficult for the hydrogen ions to react and liberate hydrogen gas, only when the current density is

increased can hydrogen gas then be liberated. This reaction occurs because the electrode/electrolyte interface is diminished in metal ions. Further details on the diffusion layer, electric double layer and electrode potentials will be given in section (3.3.6.).

When using the electrochemical series it is important to remember that the voltage is calculated from metal ions at unit activity, practically, these conditions are rarely used. If a reaction should take place from thermodynamic considerations, it doesn't mean a reaction will take place as kinetic considerations are just as important. These considerations are explained in more detail over the next few sections.

3.2 General principles of the electrochemical process

The American Society for Testing and Materials (ASTM) define electroplating as: (ASTM 2011)

> "The electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the base metal"

The electrochemical process of depositing a metal when current is applied can be seen in Figure 3.1. The electrodes are placed in the electrolyte and connected to a low voltage direct current (DC) supply, the anode is connected to the positive lead supply and the cathode is connected to the negative lead supply. Current from the DC power supply flows round the circuit as electrons to the electrolyte and then

transferred by ions to the electrode. The potential applied between the anode and the cathode controls the transfer of charge across the electrolyte interface thus determining the rate of charge transfer.

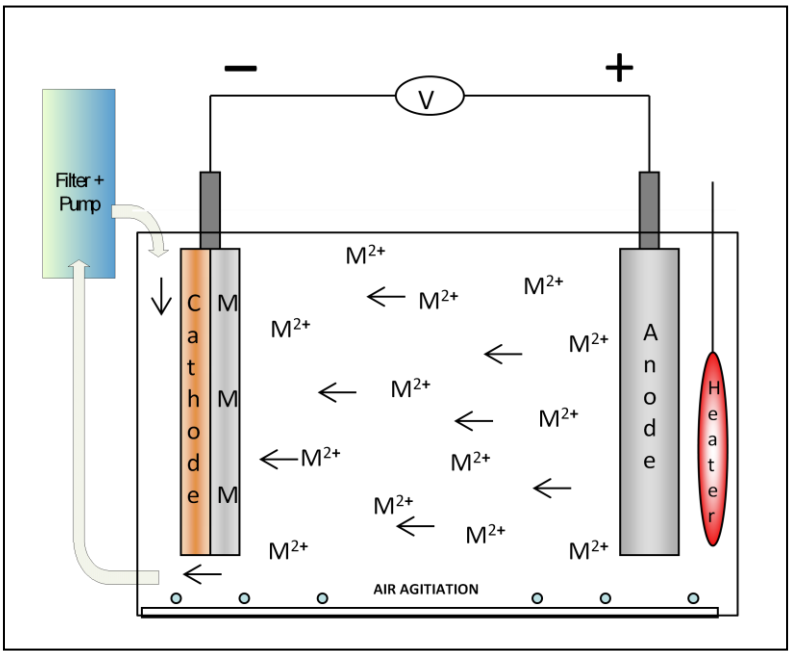


Figure 3.1 Electrodeposition of a metal in a typical electroplating tank

Typical electrolyte is composed of metallic salts (such as sulphate and chloride salts) with the use of an additive system to help brighten and level the metallic deposit (these are explained in section 3.8.2 when looking at nickel electrolytes). The metallic salts are the chemicals that dissociate into ions as in equations 3.2 and 3.3, where M is a metal atom with a +2 valency.

$$MSO_4 \rightarrow M^{2+} + SO_4^{2-} \qquad (3.2)$$

$$MCl_2 \rightarrow M^{2+} + 2Cl^{-} \qquad (3.3)$$

Diffusion will move the ions from areas of high concentration to areas of low concentration and is the primary transport mechanism. As potential is applied between the electrodes in the electrolyte the ions will also move towards the electrode with the opposite charge, electrophoresis of ions is not the primary mechanism as it is very slow. At the cathode the cations (M^{2+}) are reduced by receiving electrons (e^-) to become neutral (equation 3.4). The metal (M) is deposited onto the cathode following the shape and structure of the surface (Brown 1974).

$$M^{2+} + 2e^- \rightarrow M \qquad (3.4)$$

Simultaneously at the anode, metals become oxidised to cations, this is the reverse of equation 3.4 and is shown in equation 3.5 (Brown 1974).

$$M \rightarrow M^{2+} + 2e^- \qquad (3.5)$$

The electrons that are given up at the anode flow to the cathode, thus completing the circuit. Other side reactions may occur at the electrodes such as hydrogen gas evolution, but this can be controlled by the potential supplied or the chemistry of the electrolyte.

3.3 General principles of controlling the electrochemical process

The electrochemical process as described in 3.2 section will have a rate determining step, thus being the slowest stage in the electrochemical process; it is usually either the rate of electron transfer (supply of electrons at the electrodes) or the mass

transfer (supply of cations at the cathode). There are numerous factors that affect the rate of an electrochemical reaction and by understanding the electrochemical process the electrolyte can be controlled to optimise the deposition rate. These variables can be grouped as electrical, electrode, external and electrolyte (Walsh 1992). All the variables will be discussed in more detail over the next few sections.

Overpotential can be required to overcome various kinetic barriers, the most common is hydrogen overpotential as explained in section 3.3.1. For any reaction to take place there is a minimum amount of energy required, known as the activation energy, this can be changed in order to favour the required reaction (Lowenheim 1978) (Lyons 1974).

3.3.1 Control of the electrical variables during electroplating

The electrical variables include potential, current and charge. The potential applied to the electroplating sequence controls the rate at which electrons are transferred; the rate of this transfer controls the current. The cations can only be reduced at the rate they are diffused to the surface known as the limiting current density. Alternative reactions will take place such as the reduction of hydrogen ions as in equation 3.6, the liberation of hydrogen also known as hydrogen overpotential. By controlling the electrolyte parameters explained in this section the hydrogen and oxygen over potentials can be controlled to optimise the electrochemical process (Walsh 2000).

$$2H^+ + 2e^- \rightarrow H_2 \qquad (3.6)$$

3.3.2 Control of the electrode variables during electroplating

The electrode variables include electrode material, surface area, surface state, geometry and motion. The anode material will have an influence on the reactions taking place within the electrolyte, for instance, if an insoluble anode such as platinised titanium is used in some electrolytes, oxygen is liberated, thus increasing the concentration of hydrogen ions within the electrolyte and as a result the pH decreases (equation 3.7) (Lyons 1974).

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (3.7)$$

Other side reactions will also take place at the anode such as the liberation of chlorine if chloride salts are used in the electrolyte (equation 3.8).

$$MCl_2 \rightarrow M^{2+} + 2Cl^- \rightarrow M + Cl_2 \qquad (3.8)$$

Anodes composed of the metal required for deposition would reduce the amount of oxygen liberated and provide the electrolyte with a supply of the metallic ions as demonstrated in equation 3.9. When oxidation at the anode occurs, any impurities within the anode would then be part of the electrolyte and potentially hinder the required finish of the electrodeposited metal. For this reason any consumable anode must be of high quality and free from impurities (Canning 1982).

$$M \rightarrow M^{2+} + 2e^- \qquad (3.9)$$

Anodes of different materials have different efficiencies, if the cathodic reaction has a lower efficiency composed to the anodic reaction, then a build up of metallic ions will be produced in the electrolyte, thus hindering the process, on a commercial scale this is controlled by drag out and therefore there is no build up of metallic ions. Other reactions can involve hydrogen ions to liberate hydrogen gas (equation 3.6); the concentration of hydrogen ions in the electrolyte is diminished so the pH increases. If the electrolyte becomes too alkaline then the formation of metallic hydroxide can occur, this is insoluble and therefore will precipitate out causing numerous problems such as roughness of the electroplated deposit (Dennis 1972; Lowenheim 1978).

The surface area of the electrodes will determine the amount of current required to plate the cathode. The current divided by the surface area is known as the current density and is expressed as amperes per square decimetre (A/dm^2 or ASD), each process will have an optimum current density. The surface area of the cathode must be known so that the current required can be calculated (equation 3.10) (Canning 1982).

Plating current (A)	=	Cathode surface area (dm^2)	x	Current density (ASD)	(3.10)

The surface condition of the electrodes can influence the surface area, for instance, if there are nodules on the electrode surface it has a larger surface area compared to a polished surface. The geometry of the electrode will therefore determine areas of high and low current densities. High current density (HCD) areas are edges and high

points that protrude out, the resistance is lower at these points since the current path is short, therefore without control of the electrolyte parameters this area is prone to high current density burning which can leave a rough dull appearance. Low current density (LCD) areas are identified as recesses and the centre area of flat parts; these areas are more difficult to plate due to the higher resistance because the current path is longer (Canning 1982).

3.3.3 Control of the external variables during electroplating

The external variables during electroplating include time and agitation, Faraday's Law states that the plating time is proportional to the thickness of the metal deposited; this will be explained in more detail later in section 3.5. Agitation is used to keep a constant supply of cations at the surface of the cathode to allow constant deposition of the metal.

There are different forms of agitation including air, cathode rod movement and eductors, the principle of each method is the same. Agitation provides advantages to the electroplating process, for instance, it assists in the removal of gases from the cathode surface such as hydrogen produced at the cathode, thus reducing the co-deposition of hydrogen, which may cause hydrogen embrittlement of the substrate in zinc plating and blistering (poor adhesion of the electroplated deposit to the substrate).

3.3.4 Control of the electrolyte variables during electroplating

The electrolyte variables include temperature, pH, composition, bulk reactant concentration, and conductivity. Each variable will have an influence on the other variables as they are not independent of each other. Mass transfer is the movement of ions from areas of high concentrations to low concentrations. Within the electrolyte the ions move very slowly due to electrophoresis, the movement is largely down to convection, diffusion and conductivity. The variables listed in this section influence this movement and so the electrolyte can be controlled to achieve optimum performance. The rate determining step is the slowest step in the process and therefore the process can only happen as fast as the slowest step, electroplating processes are optimised to achieve the required finish which is not always the fastest deposition rate (Lyons 1974).

The composition of a typical electrolyte requires conductivity salts, supply of metallic ions, additives and pH control. Once the composition of the electrolyte is formulated, the concentration of each chemical becomes vital to optimising the plating process. If it becomes too concentrated the density of the electrolyte is increased, therefore movement of ions are limited and not free flowing. The ions will move slower and more likely to collide with each other instead of reducing at the cathode. If concentrations are low the density of the electrolyte is reduced and the ions can move more freely but the supply of ions at the cathode will be limited (Lyons 1974; Lowenheim 1978). Concentration, additives and alloy deposition effects require a more in depth explanation and are therefore explained later in section 3.8.

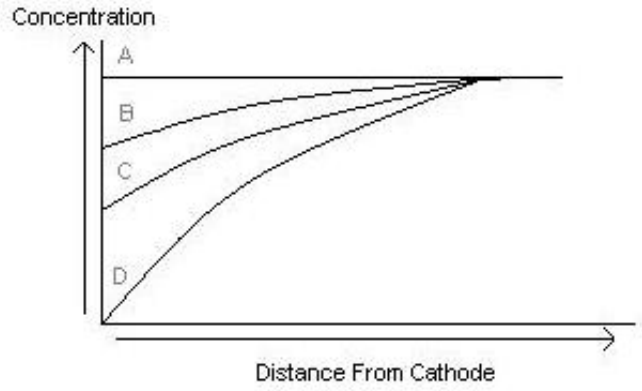
The pH of the electrolyte is determined by the hydrogen ion concentration, a higher concentration results in a more acidic electrolyte. If the electrolyte is too acidic the increased amount of hydrogen ions result in less metallic ions in the diffusion layer, thus slowing down the deposition rate. If the electrolyte becomes too alkali in the vicinity of the cathode then the metallic ions can react with the high concentration of hydroxide ions to produce metallic oxide or metallic hydroxide, which are often insoluble, thus precipitating out in the electrolyte. A buffer such as boric acid in the case of a nickel electrolyte is used to control the hydrogen ion concentration, this is achieved because the boric acid is not fully dissociated in the electrolyte, so hydrogen ions are removed from the electrolyte through electrolysis, the boric acid equalises the change in hydrogen concentration by dissolution, therefore stopping a build up of hydroxide ions.

The temperature of the electrolyte will influence the flow of ions by convection. When the electrolyte is heated the ions can move faster through the electrolyte due to the extra energy supplied. If the temperature increases above the optimum level for the electrolyte the metallic cations can move so fast that the contact they have with the cathode is reduced, slowing the plating rate down and allowing other ions to be reduced such as hydrogen ions as described in equation 3.6. If the temperature is too cold, then the ions move slowly through the electrolyte taking a longer time to reach the cathode, therefore resulting in a slower plating rate. Increased temperatures can be used to keep a higher concentration of salts in solution to maintain maximum conductivity.

The conductivity of the solution is important for the flow of electrons; this is related to the concentration of ions in solution, the chemicals used must easily dissociate in solution for it to have a high conductivity. The conductivity salts need to be at optimum concentration since a low concentration will limit the flow of ions and a high concentration will hinder the movement of ions through solution.

3.3.5 Understanding the concentration gradient in an electrochemical cell

Ions within an electrolyte will move from areas of high concentration to areas of low concentration when there is no external influence, this phenomenon is known as the concentration gradient. As an external influence is applied such as the passing of a current, this will change the cation concentration across the electrolyte. Figure 3.2 illustrates the cationic profile within the electrolyte as varying power is applied. With no current passing there is no change in cation concentration across the electrolyte. As current is applied, the concentration of cations at the surface of the cathode is reduced, the higher the current applied, the lower the cation concentration at the electrode surface due to the increased deposition rate.

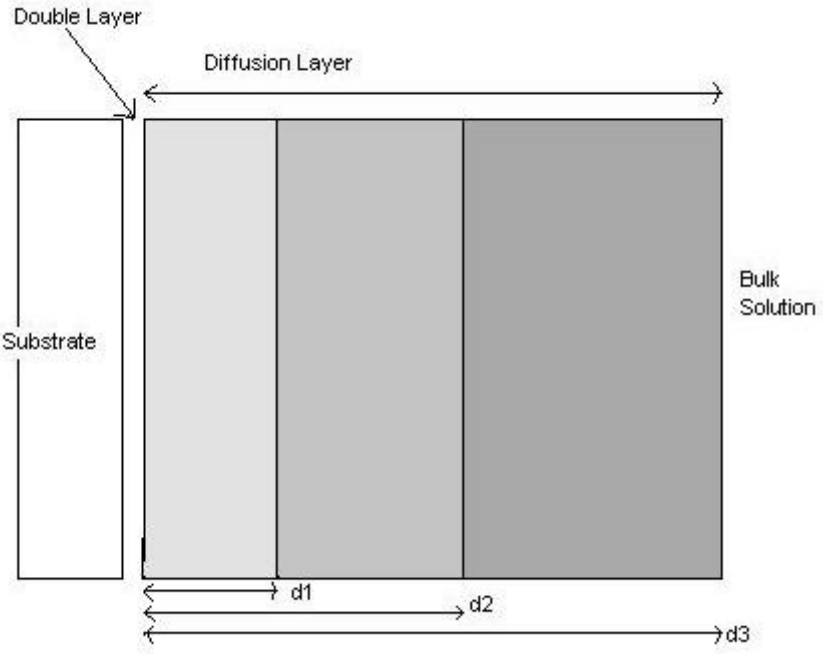


A = No passing of current the concentration will not vary with distance from cathode.
B = Low current density changes the concentration slightly with distance from cathode
C = High current density will have more of a change in concentration with distance from cathode
D = Limiting current density will have a large change with no ions at the cathode surface

Figure 3.2 - Concentration gradients (Walsh 2000)

3.3.6 Understanding the diffusion layer

The area in the electrolyte adjacent to the cathode is known as the diffusion layer, this is where the deposition of cations is controlled by the rate of electron transfer at the double layer. The quantity and movement of ions within the electrolyte will affect the diffusion layer and as a result the plating speed. Agitation, and the concentration of ions will have the largest influence on the diffusion layer for reasons explained in sections 3.3.3 and 3.3.4 respectively. Figure 3.3a illustrates the effect of agitation on the diffusion layer.



Diffusion layer thickness (d) varies with degrees of agitation.
d_1 = Vigorous agitation (thickness in order of 10^{-6}m).
d_2 = Medium agitation (thickness in order of 10^{-4}m).
d_3 = No agitation (thickness in order of 10^{-3}m).

Figure 3.3a - Diffusion layer thicknesses (Walsh 2000)

As previously explained, if the electrolyte is too concentrated the ions cannot move freely through the electrolyte, and therefore they stay surrounded by ions of the opposite charge making it difficult to accept electrons from the cathode when they move into the diffusion layer. The use of agitation reduces the diffusion layer thickness so cations become more available to the cathode. Electrolytes containing low concentration of ions will have fewer ions in the diffusion layer therefore limiting the rate of deposition.

The electrical double layer is the interface between any pair of conducting phases, for the purpose of this study it will be referred to as the interface between the electrode and the electrolyte. At the interface there is a potential difference, it is this

observed potential produced by the electrical double layer that is responsible for the properties of a given system (Roy 2013). Figure 3.3a shows the position of the double layer and Figure 3.3b shows the variation of this potential with distance from the electrode surface within the double layer. The double layer is formed by an excess of charges at the interface, this can be ions, electrons or oriented dipoles (Crow 1994).

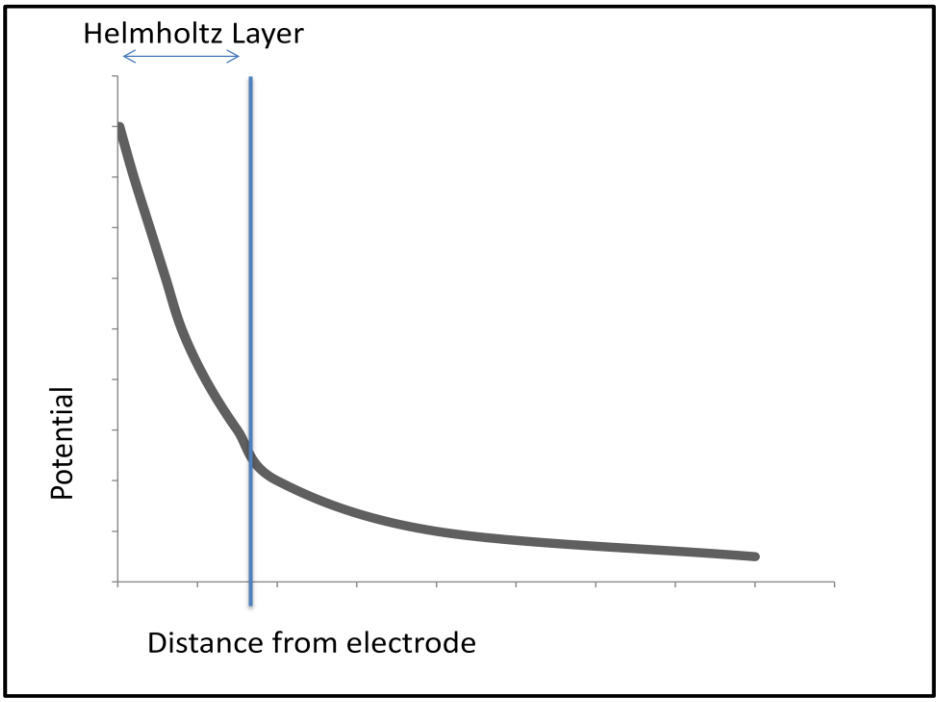


Figure 3.3b – Variation of potential with distance from the electrode surface within the double layer (Crow 1994).

Investigating the electrode placed in the electrolyte, to have electro-neutrality there must be a balance of excess charge on the electrode surface and opposite charge on the solution side, it is the distribution of the solution charge that is of importance, the standard electrode potentials are shown in Table 3.1. When electrostatic interaction operates the ions from solution can only get so close but there is no contact with the electrode because there is a layer of solvent (in this case water) known as the ‘outer

Helmholtz plane' (OHP) between the two surfaces. This region within the plane represents the compact part of the double layer called the 'Helmholtz layer' (Crow 1994, Roy 2013).

To neutralise the charge of the electrode it is not possible to fit all the required ions from solution and so the ions start to become disordered the further away from the electrode where the electrostatic forces are weaker and dispersion by thermal motion is more effective. Theoretical models of the double layer are explained in terms of electrostatic forces, and when looking at the distribution of charge, Helmholtz considered the interfacial region to be limited and the potential variation across the region was linear. Gouy and Chapman appreciated that a large area of charge in contact with the electrolyte would bring about a one-dimension charge distribution, similar to the proposal in three-dimension by the Debye-Hückel model of electrolyte behaviour. This approach is non-linear and the interfacial region extends further into the electrolyte solution to a point where the ions behave in the same way as if there was no metal introduced (Crow 1994). Gouy and Chapman suggested that a diffusion arrangement of the ions took place as this was more likely to occur; Stern and Graham have since suggested amendments to their theory taking into account the limited dimensions of ions and the presence of solvated and desolveated ions which make the two layers possible (Dennis 1972).

When considering the electrolytes used in this study the absorption of foreign ions or neutral molecules can disturb the equilibrium in the double layer. The addition of organic additives such as brighteners, levellers and surfactants are likely to produce these effects, therefore the mechanism of deposition and additive incorporation in the

deposit are closely associated with this phenomenon of the electrical double layer (Dennis 1972).

The electric field strength can be expressed as the force per unit charge experienced at the point of the electric field, measured in Newtons per Coulomb (NC^{-1}), it is equal to the potential gradient measured in Volts per meter (Vm^{-1}). At the interface the potential difference is about 0.1-1V. If the potential difference is 1V acting across a distance of 1Å (10^{-10} m) gives electric field strength of 10^{10} Vm^{-1}. This is a very strong field and therefore it causes electrons to move across the interface. In terms of an electrochemical reaction it isn't just the amount of charge there is but also the distribution and distance which determines the electric field strength and hence the speed of electron transfer between the two phases (Bockris 1972).

When electroplating the potential moves from its equilibrium and the electrode is said to be polarised, this change in potential is referred to as the concentration overpotential (Roy 2013). When an external e.m.f is applied and the current flow is fixed, the potentials of the two electrodes change from their unpolarised rate to their polarised rate, the cathode becomes more negative and the anode becomes more positive. The electrolyte adjacent to the cathode becomes depleted of cations as metal is deposited and further deposition become difficult. By looking at the Nernst equation it can be seen that the potential becomes more negative, refer to section 3.7 (Dennis 1972). When the fixed overpotential is approached (when the concentration of metal ions come near to zero) it is said to reach the limiting current density. In practice this rarely happens as other electrode processes take over, this region of localised variation of concentration is known as the anode or cathode film. There is

also a concentration gradient that takes place over these films which extend beyond the limits of the Helmholtz double layer (Dennis 1972).

3.4 Relationship between voltage, current and resistance

A German physicist, Georg Ohm (1789-1854) defined the relationship between voltage, current and resistance (equation 3.11), this is known as Ohm's law and can be used for simple circuits if the electrolyte is maintained at a constant temperature.

$$V = I \times R \qquad (3.11)$$

Where

V = Potential difference measured across the resistance in volts
I = Current through the resistance in amperes
R = Resistance of the conductor in ohms

In an electroplating cell, Ohm's law can be used to calculate the resistance. If there is an increase in resistance within the circuit, the voltage will increase. To maintain the same current, the voltage would have to be increased, thus compensating for the resistance within the circuit. An increase in resistance can be an indication that there is a problem, either within the circuit itself, polarised anodes or the conductivity of the electrolyte. This understanding can be helpful in maintaining a good working electrolyte and obtain optimum electrodeposits.

3.5 Faraday's laws of electrolysis

During the 19th century an English scientist, Michael Faraday (1791-1867) carried out research in electrochemistry and established the fundamental laws of electrolysis,

thus being the first quantitative demonstration of the electrical nature of mater, and it has long defined the quantity of electricity. (Lyons 1974; Wilcox 1992). The laws of electrolysis have remained unmodified by new discoveries and are among the foundations of physical science today (Lyons 1974). According to Crow the laws state the following (Crow 1994),

"Faraday's 1st law of electrolysis – states that in the electrolytic process, the quantity of electricity is proportional to the mass of chemical decomposition. The quantity of electricity refers to the quantity of electrical charge measured in coulombs"

"Faraday's 2nd law of electrolysis – states that the mass of an elemental material deposited at the electrode is directly proportional to the mass of the element equivalent weight at any given quantity of electricity"

Equation 3.12 summarises Faraday's laws and enables an electroplater to calculate the required amount of time and current necessary to achieve a plating thickness of the metal, as follows (Crow 1994):

$$w = \frac{i \times t \times A}{z \times F} \qquad (3.12)$$

Where

w = weight of the plated metal in grams
A = atomic weight of metal
z = valency of the metal
i = current in amps
t = time in seconds
F = Faraday constant (96500 C mol^{-1})

The Faraday constant (F) is the magnitude of electric charge per mole of electrons, the unit is coulombs per mol^{-1} (C mol^{-1}). The numeric value used is 96485.3399 but often rounded up and used as 96500. This calculation assumes 100% efficiency and gives an average weight over the cathode area. Faraday's Laws do have their limitations. Firstly, it will allow a measure of electrochemical change but it cannot explain how the change occurs and why, secondly, it does not take into account the effect of diffusion and concentration gradients nor other factors that can control the electrochemical process that have previously been explained (Crow 1994).

3.6 Butler-Volmer equation

The Butler-Volmer equation describes how the electrical current measured on an electrode depends on the electrode potential, considering that both the anodic and cathodic reactions take place at the same time. Equation 3.13 illustrates the Butler-Volmer equation (Crow 1994),

$$i = i_0 \{\exp\left[-\frac{\alpha_c \, n \, F \, \eta}{R \, T}\right] - \exp\left[\frac{\alpha_a \, n \, F \, \eta}{R \, T}\right]\} \qquad (3.13)$$

Where

i = Current (amps)
i_0 = exchange current density (A/m^2)
α = reaction order (c = cathode, a = anode)
η = overpotential
F = Faradays constant (96500 C mol^{-1})
R = gas constant (8.31 J mol^{-1} K^{-1})
T = temperature (Kelvin)
n = number of electrons

This Butler-Volmer equation is applicable when the polarisation depends only on the charge transfer kinetics, stirring the electrolyte to minimise the diffusion thickness can help minimise concentration polarisation.

3.7 Nernst equation

The Nernst equation gives the magnitude of the potential between a metal and solution of its ions. Equation 3.14 illustrates the Nernst equation (Lowenheim 1978)

$$E = E° + \frac{R\,T}{n\,F} \ln a \qquad (3.14)$$

Where

E= cell potential
E^o = standard cell potential
F = Faradays constant (96500 C mol^{-1})
R = gas constant (8.31 J mol^{-1} K^{-1})
T = temperature (Kelvin)
n = number of electrons
a = activity of the metal ion

The Nernst equation is used to calculate the voltage of an electrochemical cell or to find the concentration of one of the components of the cell. The tabulation of E^o for the elements results in the electromotive force (EMF) as shown in Table 3.1.

3.8 The composition and function of the nickel electrolyte

3.8.1 The composition and function of base salts in the nickel electrolyte

The base salts are chemicals used to add the nickel to the electrolyte in the form of both nickel chloride and nickel sulphate and also provide ions in the electrolyte also known as conductivity salts so that the electrons can flow through the solution more

freely due to the available ions. A pH buffer normally boric acid is used to control the pH within the diffusion layer during electrolysis, in the case of the nickel electrolyte if the solution becomes too alkali, nickel hydroxide forms, this is insoluble and therefore will precipitate out (Dennis 1972; Brown 1974).

3.8.2 The composition and function of additives in the nickel electrolyte

Nickel electrolytes used in today's electroplating industry have similar basic electrolyte formulations to the original Watt's bath (nickel sulphate 240g/l, nickel chloride 20g/l and boric acid 20g/l) (Dennis 1972), but the additives used in the electrolyte have been developed for a required application and tend to be confidential to the supply houses, although the generic compounds used are well known within the electroplating industry.

Additives can be categorised by their main function, as brighteners of the first and second class, levellers, stress relievers, depolarisers and wetting agents. Certain chemicals can provide more than one function. For example, an additive introduced to help relieve stress in the deposit can also help with the brightness, thus improving the appearance of the deposit (Dennis 1972).

There are two types of brighteners used in a bright nickel system, they are categorised as first and second class brighteners, these work in cooperation with each other to produce a bright lustrous finish. Class one brighteners are used in relatively high concentrations (naphthalene polysulphonic acids are used up to 15g/l and aromatic sulphonamides or sulphonimides are used at around 1.5g/l) and are identified by the conjugated alkene sulphonate group (=C-SO_2-). Figure 3.4

illustrates examples of first class brighteners. Note that these structures show the free acids but the water soluble salts can be used if the cations are not detrimental to the nickel solution.

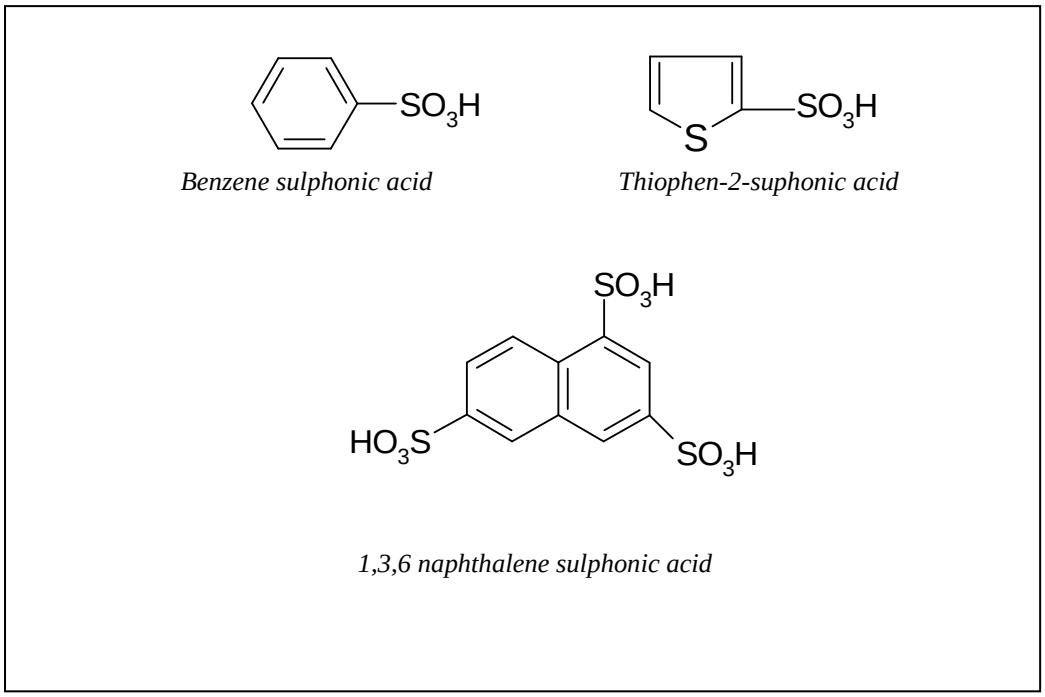


Figure 3.4. Brighteners of the first class (Dennis 1972).

Brighteners of the first class are not used independently as they do not produce a fully bright deposit and therefore require the use of brighteners of the second class. These second class brighteners are identified by the unsaturated group within the molecule (examples such as C=C, C=O, C=N, illustrations can be seen in Figure 3.5), they are used in much lower concentrations, around 0.01g/l of acetylenic compounds for example. If higher concentrations are used, the nickel deposit may become brittle and have increased tensile stress. By controlling brighteners of the second class with brighteners of the first class the concentrations can be kept to a minimum and an optimal brightness formula is produced (Brown 1974).

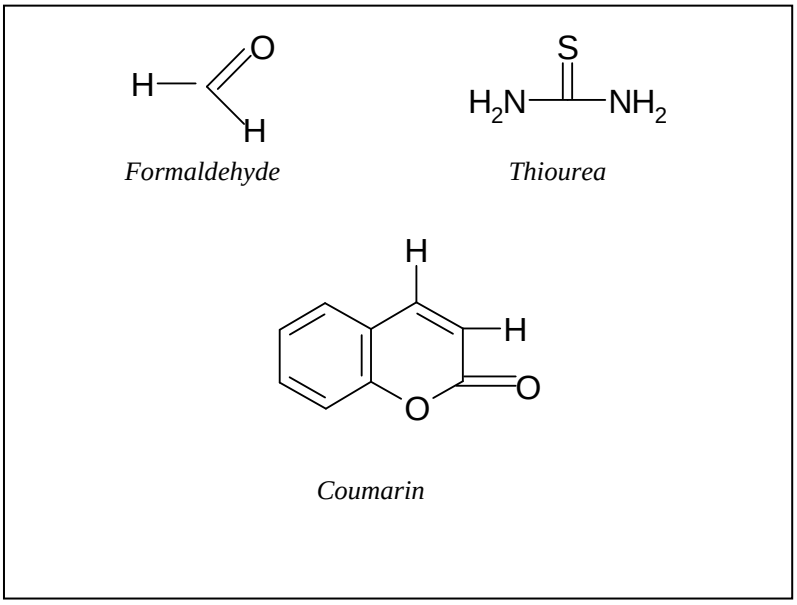


Figure 3.5. Brighteners of the second class (Dennis 1972).

Depolarisers such as thiomalic acid and thiocarboxylic acid are added to prevent skip plating. Skip playing is when areas of the substrate are not electroplated, often in recesses and low current density areas (Dennis 1972).

Stress relievers will counteract the tensile stress caused by brighteners of the second class by introducing compressive stress. Saccharin is a well known additive used in nickel plating as a stress reliever but it is also a dual function additive because it has the properties of a first class brightener (Dennis 1972; Brown 1974).

Levelling agents such as coumarin are compounds that contain no sulphur. They are used in semi-bright nickel processes to conceal any scratches and imperfections within the substrate. The leveller will slow down the nickel plating on ridges and protruding areas, thus allowing the scratched surface to be filled in first, and consequently smooth out the imperfections of the substrate (Dennis 1972; Lyons 1974).

Wetting agents are used to lower the surface tension of the electrolyte allowing any gas bubbles forming on the cathode to be released. This helps to prevent pitting of the nickel deposit. The compatibility between the additives are just as important as choosing the right ones because incompatibility can result in reduced brightness and pitting (Dennis 1972; Lyons 1974).

3.9 Characteristics of trivalent chromium electrolyte

Chromium can be electrodeposited from trivalent chromium electrolytes. In this study the decision to use the sulphate base electrolyte called TriMacIII was made due to earlier work undertaken on the corrosion rate study of different chromium electrolytes. The TriMacIII electrolyte was concluded to have a lower corrosion rate when compared to the Macrome CL3 electrolyte (Handy 2006).

The formulation for the trivalent chromium was supplied by MacDermid Plc with the following composition:

TriMacIII Conductivity salts	300g/l
TriMacIII Part 1	150ml/l
Total chromium metal	12g/l
TriMacIII Initial	10ml/l
TriMacIII Booster	0.5ml/l
TriMacIII Wetter	3ml/l

The conductivity salts enable ions to move through the electrolyte so that oxidation and reduction can take place at the anode and cathode respectively. This study has used a sulphate based electrolyte, a typical example can be found in a patent by Barclay and Deeman (Barclay 1977; Deeman 1986), the base solution consists of

potassium sulphate and sodium sulphate used to maintain a flow of ions and is not predominantly co-deposited with the chromium, but it will require monitoring as drag out can reduce the concentration of the salts, thus reducing the conductivity of the electrolyte and in turn reduce the efficiency of the process.

The chromium ions are added as chromium (III) sulphate and require a complexing agent to achieve plating. A patent by Deeman in 1986 uses a compound such as thiocyanate at a ratio between 1:1 and 1:6 of chromium to thiocyanate. The patent claims to minimise undesired gas emissions and improve efficiency and colour (Deeman 1986).

The boric acid is required as a pH buffer, since the reactions take place at both the anode and cathode the pH changes, once plating stops the pH will equilibrate to the initial pH. Other buffers can be used, for example carboxylic acid salts such as malate, formate and acetate. Additional additives known as wetting agents or surfactants can be used to help improve the coverage and plating rates while controlling the surface tension of the electrolyte (Dubpernell 1974).

3.10 Electrolytic alloy plating

Alloy plating is a widely used process to improve the properties of a metal by incorporating another metal, in some cases even numerous other metals. This can be achieved by electrolytic plating or by molten metal mixed together with other metals; this study will primarily concentrate on electrolytic plating. Alloys have been used to

replace more expensive metals such as the use of bronze as a replacement to gold and therefore an alloy will be looked at as an alternative to nickel in this study.

3.10.1 Definition of an alloy

When discussing electrodeposited alloys, Brenner in his book on the "Deposition of alloys, principles and practice" typically defines an alloy as (Brenner 1963)

> "*A simultaneous cathodic deposit that contains at least two elements of which at least one is metallic. The deposit will have metallic properties and each element cannot be visually isolated by the naked eye"*

An alloy is defined in the Oxford dictionary as the following (Oxford-Dictionaries 2010)

1. *A metal made by combining two or more metallic elements, especially to give a greater strength or resistance to corrosion.*

2. *An inferior metal mixed with a precious one.*

3.10.2 History of alloy plating

The first process for producing an alloy was by diffusion coating of zinc and copper, which was patented in England by Elkington in 1833 (Elkington 1833). The process involved immersing a copper part attached to a piece of zinc, which acted as the internal anode, into a boiling solution of zinc chloride, the process didn't involve the

simultaneous deposition of the copper and zinc and therefore was not a true alloy as defined by the Oxford dictionary. The first electroplated alloy was thought to be around the same time as the introduction of cyanide plating that is used in brass and bronze electrolytes. De Ruolz is credited with being the first to electroplate brass and bronze (Ruolz 1842), this formulation is still similar to the one used today with a cyanide complex and stannate. The brass alloy, also known as yellow copper had only one commercial application, to plate a cheaper substrate such as iron or zinc to make it appear like brass, thus reducing the cost of materials.

Brass plating was an important process according to Roseleur, who devoted 10 pages in his book to brass plating and made note to the less importance of nickel because it was five times more expensive than copper. From the late 1800's platers were looking for cyanide free solutions as the work of Professor Jacobi mentioned by Elsner,(Brenner 1963) used ammoniacal carbonate bath for depositing brass and bronze. Bronze is a copper tin alloy that can be plated to achieve either a yellow or white appearance and is still widely used today in the electroplating industry as a replacement for nickel in the jewellery industry. Today there are many patents for cyanide free brass and bronze but none are used on a large commercial scale, implying that cyanide is still the best complexing agent.

3.10.3 Theory of alloy plating

In metals that can be co-deposited as alloys require their deposition potentials to be within 0.2 volts of each other, thus limiting which metals can be alloyed together. The electrochemical series in Table 3.1 can be used as a guide, but as mentioned in chapter 1, it provides limited information since that potentials of metals can be

manipulated by changing the conditions. If the concentration of a divalent salt is changed by hundred fold, the potential will become more negative by 0.06 volts. If the concentration is reduced too much so that the more noble metal is less than 1% of the other metal, there are reproducibility problems due to the concentration changing so rapidly.

Complexing agents are widely used to change the potentials to within 0.2 volts of each other to allow alloy plating. There are different complexing agents used, a single complexant is when both metals are complexed with the same complexing ion, where a mixed complexant is when either both metals are complexed with different complexants or when one of the metals is complexed and the other is in the form of its simple ion. Complexing the metals in the electrolyte may still not bring the potentials close enough for co-deposition so changing the concentration of the complexing agent to allow free complexing ions can then help in the final adjustment, free cyanide for example can give a more negative potential (Faust 1974).

The use of complexing ions can have a secondary function by improving the metallic deposit, they can increase throwing power and change the grain structure to improve the brightness. However, they have a disadvantage as organic complexing agents, especially with a high molecular mass can cause the deposit to be stressed, cracked and brittle (Faust 1974; Lyons 1974).

Summary

This chapter describes the theory of electroplating and factors that can influence the electroplated deposit. It also details the additive system used within the nickel electrolyte and identifies the importance of the nickel deposit and its value to the electroplating industry. This chapter also explains the use of trivalent chromium as the preferred electrolyte due to previous corrosion studies.

CHAPTER 4: PRINCIPLES OF METALLIC CORROSION

Introduction

This chapter describes the principles of metallic corrosion as applicable within the remit of this study, while also explaining the fundamentals of metallic corrosion and the use of metallic coatings as a protective layer to control corrosion. A detailed explanation will be given on how nickel and chromium coatings are used to control the corrosion path and thereby increase the longevity of the deposits, and also the techniques used to accelerate and evaluate corrosion.

4.1 General principles

Corrosion is an electrochemical process that involves two reactions, 'oxidation' and 'reduction'. The oxidation reaction is where electrons are removed, also known as the anodic reaction, thus producing an actual loss of metal as metal ions are formed, as shown in equation 4.1 (Lowenheim 1978; Winston 2000). The reduction reaction, also known as the cathodic reaction is where electrons are gained, thus often converting water or oxygen to hydroxides and hydrogen ions to hydrogen depending on the environment where corrosion takes place (Shreir 1994; Winston 2000). Equation 4.2 shows the cathodic reaction of the oxygen and moisture in the atmosphere, thus being a neutral environment where oxygen is freely available and often the most likely reaction. Equation 4.3 shows the cathodic reaction in an alkali environment where hydrogen peroxide is an intermediate species. Equation 4.4 shows the cathodic reaction in an acidic environment (Winston 2000).

$$M \rightarrow M^{n+} + ne^- \quad (4.1)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (4.2)$$

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \quad (4.3)$$

$$H_2O_2 + 2e^- \rightarrow 2OH^-$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (4.4)$$

A corrosion cell consists of an anode and a cathode in electrical contact with each other and an electrolyte. The difference in potential or electromotive force (EMF) is the driving force of the reaction between the cathode and anode. Section 3.7 describes the Nernst equation that gives the potential between the metal and electrolyte, thus the reversible potential of a cathode reaction involving oxygen as given in equation 4.2 is given by equation 4.5 (Lowenheim 1978)

$$E = E^o + (0.059/2) \log [(\rho\ O_2)^{1/2} / (OH^-)^2] \quad (4.5)$$

The logarithmic term contains the oxidised species in the numerator and the reduced species in the denominator. The effective concentrations or pressures are raised to the power corresponding to their coefficients in the equation of the reaction. Putting the two half-equations together from equations 4.1 and 4.2 the complete reaction is shown in equation 4.6 (Lowenheim 1978).

$$M + ½\ O_2 + H_2O \rightarrow M^{2+} + 2OH^- \qquad (4.6)$$

The emf of the corrosion cell is the difference between the two half-cell potentials as shown in equation 4.7 (Lowenheim 1978).

$$\Delta E_{cell} = E_{cathode} - E_{anode} = E_c^0 - E_a^0 + \left(\frac{0.059}{n}\right) log \frac{(\rho O_2)^{\frac{1}{2}}}{(OH^-)^2\ (M^{+2})} \qquad (4.7)$$

The E^0 is the standard potential given in chapter 3 table 3.1 for the common metals used in electroplating. The change in free energy, ΔG, accompanying a cell reaction is given by equation 4.8 (Lowenheim 1978).

$$\Delta G = - nf\Delta E_{cell} \qquad (4.8)$$

Where

ΔG = change in free energy
ΔE_{cell} = change in potential of the corrosion cell
n = number of electrons transferred
f = faraday constant

If the reaction is to be spontaneous then ΔG must be negative and ΔE_{cell} must be positive, the higher the free-energy change, the greater the tendency for the reaction to occur. This is based on the thermodynamics, but kinetic factors will determine the rate of reaction which is important to the practical aspect when trying to slow down or limit corrosion (Lowenheim 1978).

The importance of studying the kinetics of corrosion is to: 1) Predict the corrosion rate and 2) Determine the mechanism of the overall process. The first is important to

the design and performance specification, while the second is concerned with the more fundamental search in determining the mechanism and number of steps involved in the corrosion reaction, thus, identifying the rate determining step. If the equation for corrosion is written as shown in equation 4.9 then the general rate equation will be written as shown in equation 4.10 (MacDonald 2001).

$$mM + aA + bB \rightarrow m`M` + oO + pP \qquad (4.9)$$

where,

M = Metal
M` = Metal containing corrosion products
m, a, b, m`, o, p = stoichiometric coefficients
A, B = Reactants
O, P = Products

$$r = kf\,\Theta\,[A]^{\alpha}\,[B]^{\beta} - kb\,[M`]^{\alpha`}\,[O]^{\beta`} \qquad (4.10)$$

Where

kf = Forward rate constant
kb = Reverse rate constant
Θ = Active surface area
α, β = Kinetic orders of reaction with respect to A + B reactants
$\alpha`$, $\beta`$ = Kinetic orders of reaction with respect to M` + O reactants

Once this differential rate expression has been fully defined it may be used to predict the rate of reaction (in this case corrosion) under other conditions such as temperature or reactant concentration provided that the mechanism of the reaction and the identity of the rate controlling step are unchanged (MacDonald 2001).

Analysis of the integrated form of equation 4.9 is used for practical reasons irrespective of which form is employed; reliable predictions can only be made if there is detailed information on the kinetic orders and rate constants over the range

of conditions of interest. The information of the mechanisms within the rate equation is of great value in determining the reaction process and therefore a large area of kinetic studies are used for this purpose.

According to MacDonald (2001) corrosion reactions are a heterogeneous process and therefore can be divided into three sequential processes: 1) transport of reactants to the metal surface; 2) chemical reaction of reactants with the metal and 3) transport of the products from the surface into the bulk solution. Steps 1 and 3 are referred to as "mass transfer" and step 2 as the "activation" process. In principle, by studying the rate of corrosion as a function of fluid velocity, the 3 steps described can be differentiated as shown in equations 4.11, 4.12 and 4.13 (MacDonald 2001)

Step 1, Mass transfer	$Ab \overset{Kt}{\Rightarrow} As$	(4.11)
Step 2, Activation process	$Ab + M \overset{Ks}{\Rightarrow} Ms^{n+} + As^{n-}$	(4.12)
Step 3, Mass transfer	$Ms^{n+} \overset{Kt}{\Rightarrow} Mb^{n+}$ $As^{n-} \overset{Kt}{\Rightarrow} Ab^{n-}$	(4.13)

Where

k = Rate constant
b = Bulk solution
s = Surface species
t and s on k = designate transport and surface reaction
A = Corroding species

Mass transfer is a first order process, then in the steady state the corroding species is expressed as shown in equation 4.14 (MacDonald 2001).

$$[As] = \frac{Kt\,[Ab]}{kt + ks\,\theta} \qquad (4.14)$$

The rate of reaction in terms of metal loss is therefore given by equation 4.15 (MacDonald 2001).

$$- \frac{dm}{dt} = \text{ks [As] } \Theta = \frac{ks\ kt\ \theta\ [Ab]}{kt + ks\ \theta} \qquad (4.15)$$

The rate of reaction can also be defined as the rate of appearance of metal ion in the bulk solution and expressed as equation 4.16 (MacDonald 2001).

$$\frac{d[Ms]}{dt} = \frac{ks\ kt\ \theta\ [Ab]}{kt + ks\ \theta} \qquad (4.16)$$

The fundamental properties of heterogeneous reactions in general and of corrosion reaction are illustrated in equations 4.15 and 4.16. For the rate constant kt > ks Θ the rate function is expressed in equation 4.17 and for the rate constant kt < ks Θ the rate function is expressed in equation 4.18 (MacDonald 2001).

$$- \frac{dm}{dt} = \text{ks } \Theta \text{ [Ab]} \qquad (4.17)$$

$$- \frac{dm}{dt} = \text{kt [Ab]} \qquad (4.18)$$

In equation 4.18 the rate expression no longer contains the terms for the active area or for the kinetics of the reaction at the interface, therefore the reaction is said to be completely “mass transport controlled”. Since the rates of change with time of the

two observables m and [Mb] lead to the same expression, which is independent of kt` and kt`` where the prime and double prime indicate the opposite directions of the reaction, it is clear that no information can be obtained about the kinetics of mass transfer steps which occur after the surface reaction (Prentice 1991). Analysis of data from kt` and kt`` can be obtained by studying the kinetics of the forward and reverse reactions respectively. In many cases kt is equal to ksϴ, therefore the reaction exhibits both mass transfer and activation control, in these cases the rate constant is expressed in equation 4.19 (MacDonald 2001).

$$k_{obs} = \frac{ks\ kt\ \theta}{kt + ks\ \theta} \qquad (4.19)$$

Which upon inversion give equation 4.20, this equation can be used to evaluate the ks and kt independently from the overall reaction of the hydrodynamics of the system (MacDonald 2001).

$$\frac{1}{kobs} = \frac{1}{ks\ \theta} + \frac{1}{kt\ \theta} \qquad (4.20)$$

Corrosion kinetics can be reduced to simplified forms, if two reactions follow the Butler-Volmer kinetics then the current densities of the oxidation and reduction processes are equal at the corrosion potential. If all the transfer coefficients are taken to be equal to one half, then the corrosion potential (E_{corr}) can be calculated directly as shown in equation 4.21 (Prentice 1991).

$$E_{corr} = \frac{RT}{F} \ln \left[\frac{i_{ox} \exp\left(\frac{F}{2RT}\right) E_x + i_{or} \exp\left(\frac{F}{2RT}\right) E_r}{i_{ox} \exp\left(-\frac{F}{2RT}\right) E_x + i_{oc} \exp\left(-\frac{F}{2RT}\right) E_r} \right] \quad (4.21)$$

Where

I_o = exchange current density (A/cm^2)
r = reduction process
x = oxidation process
E_x = reversible oxidation potential
E_r = reversible reduction potential

To calculate the corrosion current for a system where the reversible potentials of the oxidation and reduction reaction are far removed from the corrosion potential, the Tafel approximation can be applied to both reactions and therefore the back reaction for each process can be neglected as expressed in equation 4.22 and 4.23 (Prentice 1991).

$$i_{corr} = i_{ox} \exp \frac{\alpha_{ax} F}{RT} (E_{corr} - E_x) \quad (4.22)$$

$$i_{corr} = i_{ox} \exp \frac{-\alpha_{cr} F}{RT} (E_{corr} - E_r) \quad (4.23)$$

To obtain the corrosion potential based on the magnitude of the corrosion current density and each component is a positive quantity, this can be achieved by using the right hand side of equation 4.22 and 4.23, as shown in equation 4.24 (Prentice 1991).

$$E_{corr} = \frac{\left(\frac{RT}{F}\right) \ln \frac{i_{or}}{i_{ox}} + \alpha_{cr} E_r + \alpha_{ax} E_x}{\alpha_{ax} + \alpha_{cr}} \quad (4.24)$$

If the transfer coefficients are assumed equal to one half, then equation 4.23 can be further reduced. When the exchange current densities for the reactions are equal, the logarithmic becomes zero and the corrosion potential is the average of the reversible potentials of the two reactions. By substituting equation 4.22 into equation 4.24 an expression can be obtained for the corrosion current density in terms of the kinetic parameters and the reversible potentials. If the transfer coefficients are taken to be equal to one half, then the following simplified expression is shown in equation 4.25 (Prentice 1991). The kinetic expressions derived in this section are all valid at the corrosion potential and corresponding current density (Prentice 1991).

$$i_{corr} = (i_{ox}\, i_{or})^{1/2} \exp\left[\frac{F}{4RT}\,(E_r - E_x\right] \qquad (4.25)$$

Corrosion products depend on the metal involved and the environmental conditions (Lowenheim 1978). As an example, Shreir (1994) has shown that in most environments the ferrous ions and hydroxide ions combine to form ferrous hydroxide as shown in equation 4.26 (Shreir 1994).

$$Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \qquad (4.26)$$

Shreir (1994) and Movchan (2005) have shown that iron can then be further oxidised to iron (III) in wet or moist environments. Equation 4.27 shows the formation of the iron (III) oxide-hydroxide. Equation 4.28 shows the formation of iron (III) oxide. These products are commonly known as ‘rust’ (Shreir 1994; Movchan 2005).

$$4\ Fe + 3O_2 + 2H_2O \rightarrow 4\ FeO(OH) \quad (4.27)$$

$$2\ FeO(OH) \rightarrow Fe_2O_3.H_2O \quad (4.28)$$

The iron (II) and iron (III) compounds have poor adhesion to the surface of the iron and easily flakes off, thus, exposing iron underneath. The exposed iron then continues to react with the atmosphere until all the iron is oxidised.

As electrochemical corrosion takes place the surface of the metal becomes an area of electrochemical cells where oxidation and reduction are taking place. It is here where anodic and cathodic areas are produced and allow current to flow. This potential difference can be found where there are areas of stress, composition or temperature difference, scratches or pits (Shreir 1994; Smith 1998). As the metal continues to corrode, the anodic and cathodic areas change, thus eventually consuming the whole surface of the metal. (Shreir 1994).

4.2 Controlling metallic corrosion

Metallic corrosion is an electrochemical process as explained above. This is a process that is often undesirable, but in some circumstances it can be used as an advantage. Steel ships will corrode when in contact with sea water, to prevent this process; sacrificial anodes (zinc blocks) are placed on the bottom of the ship. A explained by Channing (1982) and Shaw (2006) the zinc has a more negative electrochemical potential and therefore corrosion will take place on the zinc blocks,

this is known as sacrificial protection and will protect the steel even if the coating contains discontinuities (Canning 1982; Shaw 2006).

The electroplating industry provides electrodeposited coating to protect a corrodible base and/or provide an attractive finish to a cheap substrate. Taking the automotive industry as an example, the interior section of a vehicle is mainly plastic: thus being easy to mould; corrosion resistant; cheap; but aesthetically displeasing. The process of electroplating allows the use of plastics while giving an attractive finish. There is a consequence to this process; the finish is often metallic which will eventually corrode.

There are numerous factors to consider when electroplating for corrosion resistant purposes. The pre-treatment of the substrate before electroplating is important to provide a clean surface so good adhesion of the electroplated deposit can be achieved. The thickness of the deposit needs to be sufficient so not to be porous, but, not too thick that it becomes too expensive or impractical. The deposit is often formulated to reduce stress in the deposit so to prevent cracking. Shreir (1994) has concluded that the substrate should have an even distribution of deposit, thus, reducing any thin and weak areas in the deposit where corrosion can take place (Shreir 1994).

Industries invest heavily in research to slow down or control the corrosion process. The choice of material used is dependent on numerous factors, these include: cost, practicality and corrosion resistance. When looking at metallic coatings the

mechanical, physical and chemical properties are considered with the understanding that these may change if the environment which they are used in changes.

4.3 The corrosion protection provided by the electroplated nickel deposit

Developments have been made to increase the corrosion protection of the substrate by introducing subsequent nickel layers as a duplex nickel system. Dobrev (1986) and General Motors (2010) have demonstrated that the automotive and sanitation industry for example use the duplex nickel principle to increase the corrosion protection of the substrate (Dobrev 1986; General-Motors 2010). This method involves two layers of nickel, the first being a semi-bright nickel which is plated directly onto the substrate, and the second being a bright nickel. The semi-bright nickel layer is essentially sulphur free whereas the subsequent bright nickel layer contains substantial amounts of sulphur due to the additives added (primarily saccharin). The reasoning behind this process is to increase corrosion protection and control the corrosion when it starts, this is achieved by the bright nickel layer corroding preferentially to the semi-bright nickel layer (Brooman 2001).

The bright nickel layer will corrode in the normal manner by pits penetrating through to the semi-bright nickel layer, the semi-bright layer is more noble so the corrosion starts to spread laterally along the bright nickel layer and forming flat bottomed pits instead of going straight through to the substrate as demonstrated in Figure 4.1 (Tremmel 1996; Brooman 2001). The appearance is still acceptable when compared to the pits penetrating down to the substrate causing blisters and discolouration from corrosion of the substrate metal. This process will slow down corrosion but not

eliminate it. If long exposure in a corrosive atmosphere is maintained then eventually the semi-bright layer will be attacked and blisters will form on the substrate metal.

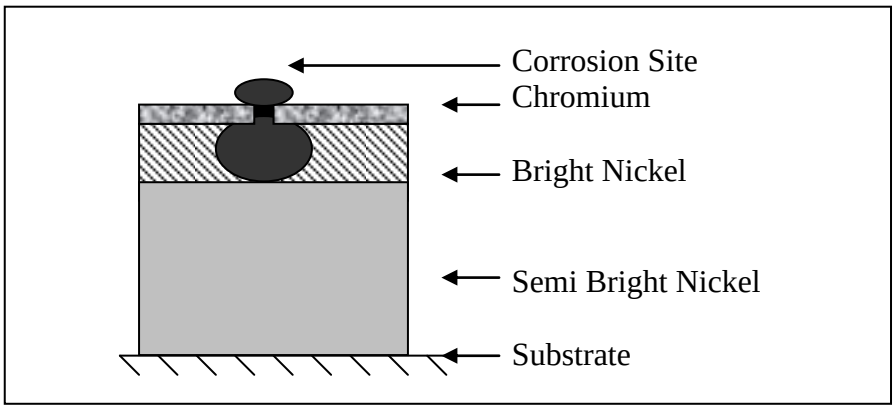


Figure 4.1. Corrosion attack through the duplex nickel (not to scale)

The specification ISO 1456 2003 refers to other types of chromium coatings which are achieved by a third nickel layer plated on top of the bright nickel, they are known as micro-porous and micro-cracked nickel. The micro-porous nickel contains inert non-conducting particles which are co-deposited with the nickel at a thickness of about 1-2µm, the number of pores should be in the region of 10’000 per square centimetre (General-Motors 2010). The chromium is then plated on top and because the particles are inert and non-conducting the chromium will not plate over them. The micro-cracked nickel is formulated to produce a high tensile stress within the deposited nickel. This quickly exceeds the ultimate tensile strength of the coating and so cracks are spontaneously formed. The chromium is then plated onto the nickel at a thickness of 0.8µm to achieve the required stress to expose the cracks, if the chromium is plated too thick the cracks could be covered over. There should be at least 250 cracks per square centimetre once the chromium is plated onto the nickel (General-Motors 2010), there can be a loss of appearance with the chromium finish

with the use of micro-cracked or micro-porous nickel layer because the chromium is not completely uniform due to the nickel underneath.

When a third nickel (micro-porous or micro-cracked) is introduced onto the bright nickel this layer is more noble than the bright nickel layer which will corrode first. The micro-porous layer provides areas in the chromium layer so the corrosion sites are spread over the surface to stop localised corrosion as demonstrated in Figure 4.1. Figure 4.2 shows the spread of corrosion with the use of micro-porous nickel.

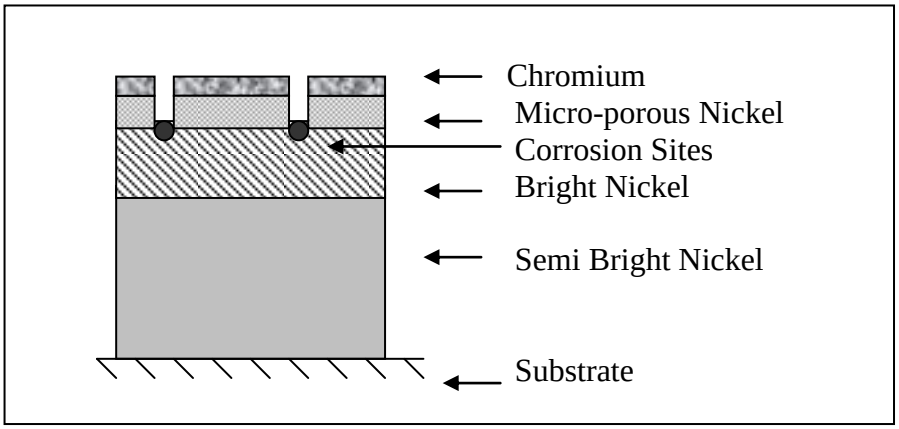


Figure 4.2. Corrosion attack through the triple nickel layer (not to scale)

The fourth nickel layer that can be introduced into the sequence is a high sulphur nickel layer plated directly onto the semi bright nickel. The high sulphur nickel is the least noble nickel layer of the sequence but will have some protection from the bright nickel layer above. The idea is that corrosion will penetrate deeper into the nickel layers and stop visual defects plus with the extra nickel layers, corrosion to the base metal is slower. Figure 4.3 shows the corrosion attack through the four nickel layer sequence.

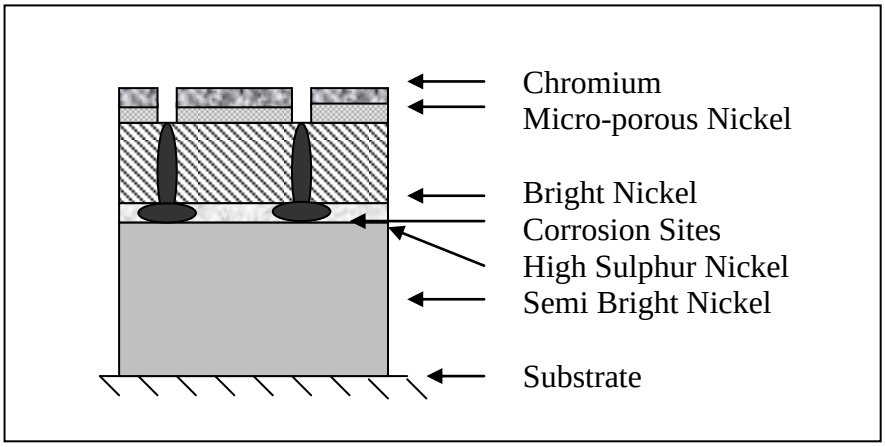


Figure 4.3. Corrosion attack through the four nickel layers (not to scale)

The following example has been taken from a specification used for electrodepositing coatings of nickel plus chromium (ISO 1456 2003). The first layer plated directly onto the substrate is a semi bright nickel, this will have a sulphur content of <0.005 % mass fraction with 50-70% of the overall nickel thickness. The next layer is a high sulphur nickel containing a sulphur content of >0.15% mass fraction and a thickness of ≤10% of total thickness. The third layer is bright nickel with a sulphur content of >0.04% and <0.15 % mass fraction, the thickness is required to be ≥30% of total thickness. The fourth layer is either the micro-cracked or micro-porous nickel, they are used in the same way as described above. The chromium is then plated as the final layer, thus usually with a minimum thickness of 0.3µm (General-Motors 2010).

Chromium is an active metal and forms an oxide layer, thus being more noble than nickel and therefore offers better corrosion resistance, the nickel layer is required due to the chromium being porous as it is only plated to a thickness of 0.3µm to provide an acceptable appearance. If the nickel layer was to be eliminated the chromium would need to be at least plated to 10µm, thus reducing porosity of the

deposit but hindering the bright appearance and also increasing the stress within the chromium deposit. Using nickel and chromium together gives the best possible finish for numerous applications and maintaining corrosion protection to the substrate.

4.4 Techniques to measure and evaluate corrosion

There are numerous techniques used to measure and evaluate the effect of corrosion on a metal. The electroplating industry use selected methods and specification to maintain consistency and therefore comparisons can be made between results. These specifications are widely accepted as standards and are used for both research and quality control purposes.

Corrosion can be a very slow process and therefore to evaluate a metal's rate of corrosion in real time is impractical. Accelerated salt spray corrosion tests have been developed to speed up the corrosion process by exposing the metal under test to controlled corrosive environments, studies by Figueiredo et al and Rossi et al use the ASTM B-117 salt spray specification for their corrosion work on bronze materials (Rossi 2003; Figueiredo 2007; ASTM 2009). This allows a corrosion test to be carried out over a number of hours or days and not months or even years. Although the results cannot be correlated with real time, it is used as a comparison with other materials tested under the same conditions. A more detailed explanation of accelerated salt spray testing can be found in chapter 5.

Electrochemical testing such as Electrochemical Impedance Spectroscopy (EIS) is a valuable method for determining the corrosion resistance of a material. The electrochemical cell is represented by a series of resistors and capacitors interpreted from the impedance spectrum, thus allowing the interpretation of the corrosion behaviour and corrosion rates. A study by Rossi et al uses EIS to compare Nickel/PTFE to Bronze/PTFE, the study concluded that the Nickel/PTFE had better corrosion protection properties (Rossi 2003). A study by Bostan et al uses EIS to determine if inhibitors help improve the corrosion resistance of bronze and optimise the concentration of the inhibitors (Bostan 2012). Figure 4.4 show the Nyquest plots from the EIS data in Bostan's study.

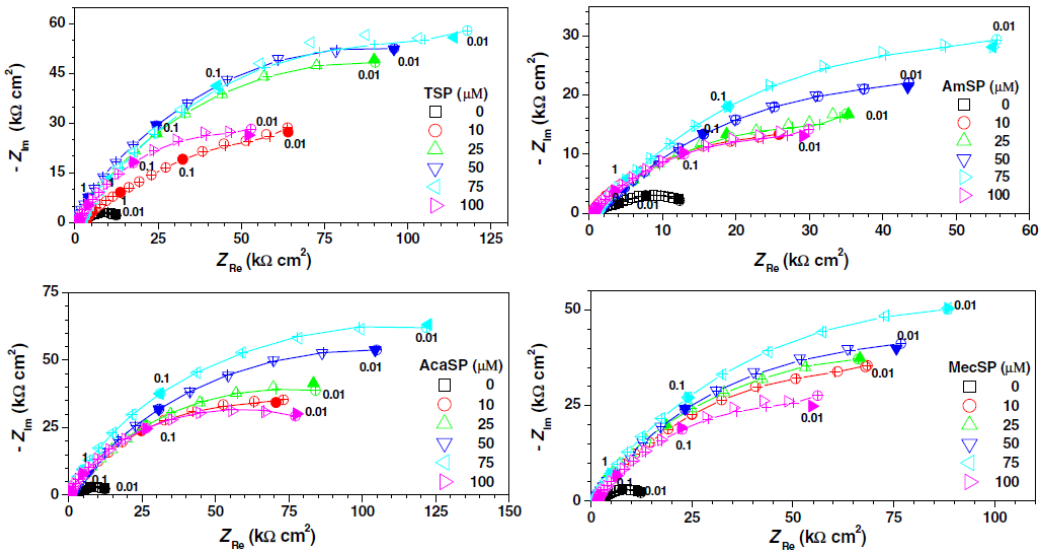


Figure 4.4. Nyquest impedance diagrams of bronze electrode in $Na_2SO_4/NaHCO_3$ (pH5) solution without and with various concentrations of phenothiazine derivatives. Frequencies are expressed in Hz. (Bostan 2012)

Further detail of EIS and other electrochemical techniques (linear polarisation) can be found in chapter 5.

Characterisation of the materials surface before and after corrosion can be a useful tool: this can identify corrosion cells produced; localised corrosion sites and provide information on the path of corrosion. The Scanning Electron Microscope (SEM) and Atomic Force Microscopy (AFM) are established instruments used for this purpose and explained in more detail in chapter 5. Rossi et al uses the SEM to identify an even and uniform Nickel/PTFE deposit and to demonstrate that the zinc phosphate deposit has a highly irregular surface, which is shown in Figure 4.5. Chiavari et al uses both the SEM and AFM techniques to evaluate the nature and morphology of the corrosion products on two types of bronzes (Chiavari 2006).

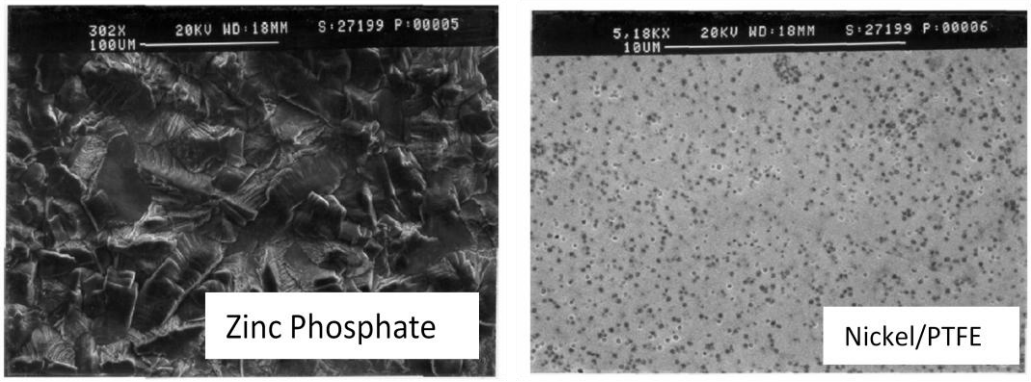


Figure 4.5. SEM images of Zinc Phosphate and Nickel/PTFE deposits. (Rossi 2003)

Spectrophotometry is used to measure colour as a numeric value, this can be applied to numerous applications, it is a highly accurate measurement and not always used in corrosion related studies (Vaughn 2009). A study by Luciano et al used spectrophotometry, CIB L*a*b* colour space, to characterise the bronze monuments with relation to the natural cleaning and weathering effect of patinas and coatings (Franceschi 2006; Luciano 2009). Spectrophotometry can also be used as a tool to help match a specific colour when using an alternative material as demonstrated by

Hingley et al (Hingley 2011). A full explanation of spectrophotometry and the CIB L*a*b* colour space is given in chapter 5.

Summary

This chapter has explained the general principles of corrosion and demonstrates how the electroplating industry manipulates the path of corrosion to increase the life of the nickel and chromium electroplated deposits. Techniques used within the electroplating industry to evaluate corrosion have been described, these include: accelerated salt spray tests; electrochemical test (EIS) and surface analysis using SEM and AFM techniques. Spectrophotometry is also a valued technique when investigating a change in appearance, whether due to corrosion products or finding an alternative material with the same appearance. This study uses a combination of the techniques mentioned to give a more comprehensive evaluation and compare the rate of corrosion. Each technique mentioned is a valuable tool in the evaluation of corrosion and relevant to this study but by no means a comprehensive list of techniques.

CHAPTER 5: RESEARCH METHODOLOGY

Introduction

This chapter outlines the research methodology used in this study which seeks an alternative to nickel compounds used for deposition in the light of the reclassification as a suspected carcinogen. This includes the methodology for electroplating nickel, yellow and white Cu-Sn alloy and chromium. The techniques used to characterise the deposits are also detailed in this chapter, these include spectrophotometry to evaluate the colour of the deposit, scanning electron microscopy and atomic force microscopy used to evaluate the deposit structure and topography, electrochemical impedance spectroscopy and linear polarisation technique to evaluate the corrosion resistance electrochemically and also neutral salt spray and copper accelerated acetic acid salt spray to assess the corrosion resistance of the deposit in an accelerated corrosive environment.

5.1 The formulation and operating parameters for the electrolytes used in this study

All the commercial electrolytes used to complete this study were electroplated by the researcher (S Hingley) using the demonstration plant and chemicals supplied by MacDermid Plc, Birmingham, UK. To maintain confidentiality the raw materials used to prepare the salts and additives of the different electrolytes cannot be published. Formulations will be given for similar electrolytes from other published sources to provide the relevant information required for this research.

Each electrolyte requires a maintenance program to sustain the optimum concentrations of each chemical component, for this study the electrolytes were not used continually for long periods of time and therefore required very little maintenance. A technical data sheet (TDS) is supplied with each electrolyte and outlines the maintenance procedure required for long term continual use and can be obtained from MacDermid Plc, Birmingham, UK.

To maintain consistency in the deposit under test, nine brass panel substrates (panel size 10 × 7.5 × 0.05 cm) were plated at the same time on the same jig. This enabled accuracy of the deposits composition and thickness and therefore limited the variability in deposition. Accurate and reliable results were therefore obtained from all tests carried out within this study. This was done to eliminate any inconstancies that can arise when electroplating due to a change in variables as explained in chapter 3. The Cu-Sn alloy deposit was required to have a specific composition that remained consistent for all the tests carried out within this study. The use of the scanning electron microscope established the correct Cu-Sn alloy so to maintain reliable and accurate comparative results and be able to compared the results with those of the nickel deposit. The thickness required for all the deposits electroplated was important for the accuracy of the results, therefore, this was checked using a Couloscope in accordance with the ASTM B 764-94 (ASTM 2009).

5.1.1. The formulation and operating parameters for the pre-treatment electrolytes

To obtain an optimum finish and good adhesion from the nickel and chromium deposits, the substrate needs to be free from any oil, dust and general dirt, the presence of any impurities could cause accelerated corrosion and hinder the visual appearance. The method of pre-treatment is determined by the material of the substrate. In this study the substrate used was a polished brass panel (10 x 7.5 x 0.05cm) and the pre-treatment used to clean the brass panel involved a three stage process as described below. Figure 5.1 is a photo of the Metex PS Activax cleaning tank in MacDermid's process development centre.

Stage 1: **Metex PS Activax** – This is an alkali cathodic electrolytic cleaner used to remove oils, water soluble lubricants and buffering compounds, it is supplied as a salt and is made up to a concentration of 25g/l with water. The solution requires stainless steel anodes and is operated at 80^{o}C, the brass panels are cleaned for 3 minutes at 3amp/dm^{2} then rinsed with deionised water (MacDermid 2007).

Stage 2: **Metex PE E5** – This is an alkali anodic electrolytic cleaner used to apply an oxide coating onto the substrate surface so when it is removed during stage 3, any contamination left on the surface from stage 1 will be removed. The working solutions is optimised at a concentration of 30g/l of the salts supplied and operated at 80^{o}C with a stainless steel cathode, the brass panels are cleaned for 3 minutes at 2amp/dm^{2} then rinsed with deionised water (MacDermid 2006).

Stage 3: **Metex M-629** – This is an acid dip cleaner which also contains activators and surface active agents to optimise the substrate surface before electroplating, this stage will remove the oxide layer previously deposited and any other residue. It is supplied as a salt and made up to a concentration of 90g/l with deionised water and used at room temperature; the brass panels are dipped in solution for 3 minutes then rinsed with deionised water (MacDermid 2001).

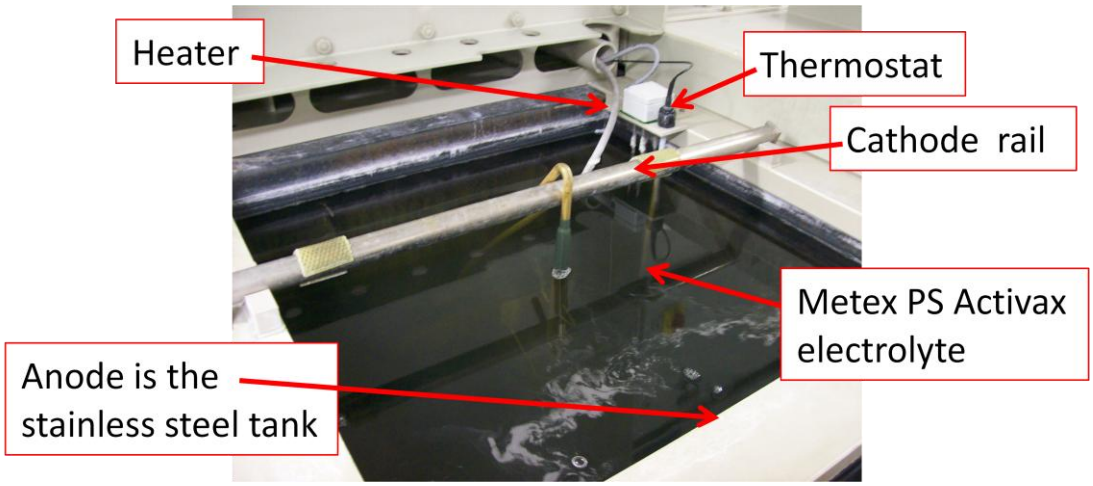


Figure 5.1 MacDermid's Metex PS Activax cleaning tank from their process development centre.

5.1.2. The formulation and operating parameters for the nickel electrolyte

The nickel deposit is electroplated onto the substrate directly after pre-treatment to obtain the optimum adhesion, thus providing the best finish for corrosion protection and visual appearance. The process supplied was NiMac Clarion II, this process is very receptive to chromium while offering good levelling to even out any small imperfections in the substrate. The deposit is also ductile and provides a bright finish across all current density areas. Figure 5.2 is a picture of the nickel tank in the MacDermid's process development centre. Table 5.1 provides the optimum makeup

of salts and additive for NiMac Clarion II, while Table 5.2 provides the function of the salts and additives in this process. The NiMac Clarion II is operated at 55^{o}C, pH 4.2, requires air agitation, high purity nickel anodes and the substrate is plated at a current density of 4 A/dm^{2} giving a plating speed of 0.8µm/minute (MacDermid 2006).

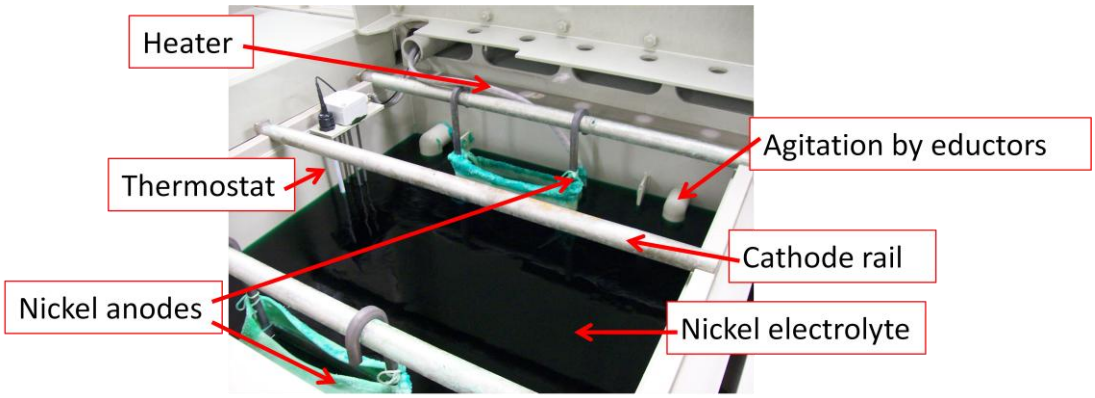


Figure 5.2 MacDermid's nickel plating tank in their process development centre.

NiMac Clarion II electrolyte composition	**Concentration**
Nickel metal	78g/l
Nickel sulphate hexahydrate	270g/l
Nickel chloride hexahydrate	75g/l
Boric acid	45g/l
NiMac 14	14ml/l
NiMac 33	30ml/l
NiMac Clarion II	1.2ml/l
NiMac 32C	1ml/l

Table 5.1. Composition of NiMac Clarion II (MacDermid 2006).

NiMac Clarion II additive	Function of the additive
NiMac Clarion II	Provides the brightening and levelling of the deposit.
NiMac 33	Improves the ductility and throwing power of the deposit.
NiMac 14	Work in conjunction with NiMac Clarion II additive to optimise the brightness and levelling of the deposit.
NiMac 32C	This is a wetting agent used to maintain the surface tension of the electrolyte.

Table 5.2. The function of the additives used in the NiMac Clarion II electrolyte (MacDermid 2006).

It is important to maintain the electrolyte and keep the salts and additives at the correct concentrations. If there is an imbalance in the formulation the deposit can be compromised. Visual problems such as a dull hazy deposit, poor levelling or throwing power can easily be seen if the electrolyte becomes overdosed or underdosed, analysis of the additives are often carried out to maintain the correct concentrations.

5.1.3. The formulation and operating parameters for the trivalent chromium electrolyte

The trivalent chromium is electroplated onto the nickel deposit to give the final appearance required and improve corrosion resistance. The electrolyte used was TriMacIII, and was developed to replace hexavalent chromium based process due to health and environmental concerns outlined in chapter 3. The TriMacIII process offers the typical light chromium colour similar to the deposit from a hexavalent process and with improved deposit distribution. To obtain the optimum deposit the electrolyte is maintained at pH 3.5 and requires air agitation. The anodes used are

TriMacIII insoluble anodes and the panels are plated at 10 A/dm^2, thus giving a plating rate of 0.03µm/minute. Figure 5.3 is a photo of the TriMacIII plating tank from MacDermid's process development centre. Table 5.3 lists the makeup formulation and Table 5.4 describes the function of the additives for this process (MacDermid 2009).

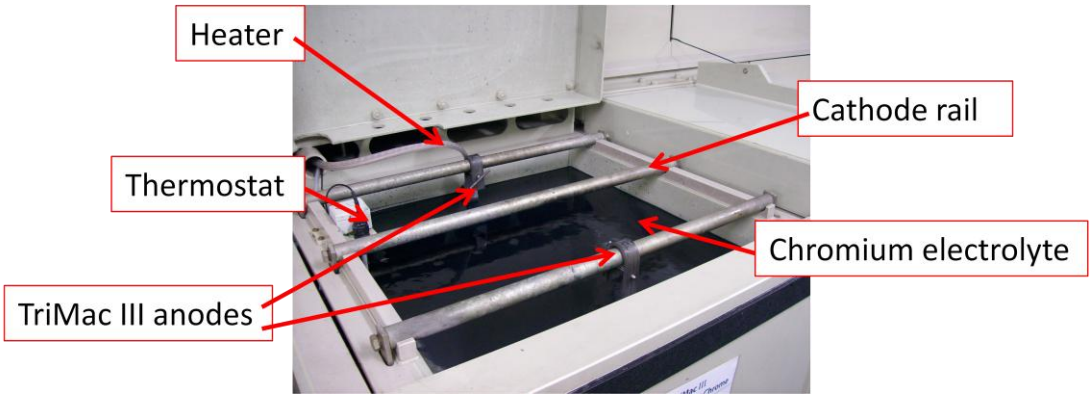


Figure 5.3 TriMacIII plating tank from the MacDermid process development centre.

TriMacIII electrolyte composition	**Concentration**
TriMacIII Conductivity salts	300g/l
TriMacIII Part 1	150ml/l
Total chromium metal	12g/l
TriMacIII Initial	10ml/l
TriMacIII Booster	0.5ml/l
TriMacIII Wetter	3ml/l

Table 5.3. Formulation for the makeup of TriMacIII electrolyte (MacDermid 2009).

TriMacIII additive	Function of the additive
TriMacIII Part 1	Maintains the chromium concentration.
TriMacIII Part 2	Maintains the deposits colour and plating rate.
TriMacIII Initial	Maintains optimum performance, once running it can be maintained at 5ml/l.
TriMacIII Booster	Used after a period of shutdown to restore optimum performance.

Table 5.4. Additives used to maintain an optimum deposit using the TriMacIII process (MacDermid 2009).

The TriMacIII process is susceptible to metallic contamination including nickel, copper and iron, to reduce the build up of these contaminants, good rinsing is required between the different electrolytes. If the electrolyte does become contaminated then a process of ion exchange can be carried out, this is where the electrolyte passes over a selected resin which takes out the metallic ions from the electrolyte, thus purifying the solution. Dummy plating can be carried out as ion exchange can become expensive but this method is time consuming on a production plant, and therefore not always cost effective.

5.1.4. The formulation and operating parameters for the copper electrolyte

The electrodeposition of copper was from an electrolytic process called CuMac Crystal, electroplated copper offers similar properties to nickel in terms of being a ductile, bright appearance with high levelling capability. A visual difference between the nickel and copper deposit is the colour (nickel is silver in colour and copper is orange in colour), it is used in this study to replace the nickel layer, in combination with the Cu-Sn alloy deposit. Copper was eliminated as a direct replacement because of the contamination risk to the trivalent chromium and the lower corrosion protection it provides (Simon 1997).

The CuMac Crystal is operated at 25^{o}C with air agitation, the average cathode current density is 3 A/dm^{2} and it is plated until the required thickness is obtained at an average rate of 0.6µm/minute. Table 5.5 lists the formulation required to make-up the electrolyte and Table 5.6 presents the function of each additive (MacDermid 2006).

CuMac Crystal electrolyte composition	**Concentration**
Copper sulphate	220g/l
Sulphuric acid SG 1.84	33ml/l
Chloride	80mg/l
CuMac Crystal brightener	1.0ml/l
CuMac Crystal leveller	0.75ml/l
CuMac Crystal wetter	0.5ml/l

Table 5.5. Formulation for the makeup of CuMac Crystal electrolyte (MacDermid 2006).

CuMac Crystal additives	**Function of the additive**
CuMac Crystal brightener	Provides excellent brightness and throwing power of the deposit.
CuMac Crystal leveller	Increases levelling capability and improves low current density performance.
CuMac Crystal wetter	This is an optional additive used if the deposit shows pitting.

Table 5.6. Additives used to maintain an optimum deposit using the CuMac Crystal process (MacDermid 2006).

It is recommended that the chloride concentration is maintained between 70-100mg/l to keep the deposit's brightness and maintain optimum levelling. Working the electrolyte at higher temperature will consume the additives faster resulting in more frequent additions.

5.1.5. The formulation and operating parameters for the yellow Cu-Sn alloy electrolyte

The yellow Cu-Sn alloy was electrodeposited directly onto the copper deposit with an average plating rate of 0.8µm/minute when plated at 50^{o}C and at a current density of 4 A/dm^{2}. Agitation is not required whilst plating, although when not in use the occasional agitation is required to stop layering of the solution. Table 5.7 represents a yellow Cu-Sn alloy formulation (Brenner 1963).

Yellow Cu-Sn alloy electrolyte composition	**Concentration**
Copper cyanide	29g/l
Sodium stannate	20g/l
Sodium cyanide	65g/l
Sodium hydroxide	7.5g/l

Table 5.7. Formulation for the makeup of a yellow Cu-Sn alloy electrolyte.(Brenner 1963)

5.1.6. The formulation and operating parameters for the white Cu-Sn alloy electrolyte

The white Cu-Sn alloy deposit is electroplated directly onto the copper or the yellow Cu-Sn alloy deposit depending on the required plating sequence. The formula supplied by MacDermid was Starvet, and marketed as a final top layer, it is a bright, white coloured deposit used in decorative applications where nickel cannot be used. The average plating rate of Starvet is 0.2µm/minute when plated at 50^{o}C with a current density of 1 A/dm^{2}.

Mechanical agitation is required for this process, since air agitation reduces the amount of free cyanide within the electrolyte (Brenner 1963). Table 5.8 shows a white Cu-Sn alloy formulation similar to Starvet.

White Cu-Sn alloy electrolyte composition	**Concentration**
Copper cyanide	11g/l
Sodium stannate	94g/l
Sodium cyanide	27g/l
Sodium hydroxide	10g/l
Sodium potassium tartrate	37g/l

Table 5.8. Formulation for the makeup of a white Cu-Sn alloy electrolyte. (Brenner 1963)

There are no additives for white Cu-Sn alloy plating because it relies on the bright copper finish underneath, Starvet does use an additive called Starvet Brillantante as a brightener and is not always required on new make ups. Starvet Brillantante was not used in this study.

5.2 Analytical techniques for the evaluation of electroplated deposits

The colour of a deposit can change across the current density areas of the electroplated panel due to the characteristics of the additives used and the deposit thickness. This effect has been limited by controlling the electrolyte in accordance with the TDS and plating all the brass panels together to reduce variability within the plating process is reduced. The nature of electroplating will always give some variability, therefore, to minimise any effect on colour each electroplated panel had three colour readings taken over three areas of the panel (high, medium and low

current density areas) and the mean average was taken. This process was carried out for each electroplated deposit used in this study.

5.2.1 Colorimetry (significance of colour identification of the deposit)

Colour analysis is made up of three attributes, hue, lightness and saturation, by bringing the three attributes together a colour is identified, if the colour is slightly changed, the attributes change, thus giving a very wide range of colours (Konica-Minolta 1998; Vaughn 2009).

Hue: *is the colour as we see, the sky is blue and the grass is green for example. When colours are mixed such as yellow and red we see orange, this is the basis of a colour wheel.*

Lightness: *is used to describe how bright a colour is, it can be independently valued regardless of its hue, thus allowing another dimension to colour.*

Saturation: *the more saturated a particular colour the more vivid it appears, objects are very rarely one colour as explained by the hue.*

Colour is affected by a variety of conditions, the light-source, background, direction of light that reflects off the object, size of the object and the observer, these factors can influence how an object is perceived, therefore making it difficult to be consistent when describing colour. Detailed information on the effects of the variables on colour are described by Konica Minolta (Konica-Minolta 1998).

Light source: *Sunlight, fluorescent light, tungsten light are examples of different light source and will make the same object look a different colour, the light sources are often referenced to when describing colour in order to be consistent when comparisons are made.*

Background: *A bright background can make the object look dull and vice versa, this is referred to as contrast effect, for example the background colour can make an object appear less vivid when it is a similar shade.*

Directional: *The angle at which the object is observed can determine how bright the colour is perceived. The directional characteristic is determined by the colouring materials, the direction of the illumination and angle from which it is viewed must be constant for accurate colour evaluation.*

Size: *A small object can appear dull compared to the same colour on a larger object; this is referred to as area effect.*

Observer: *Each person has a different sensitivity to colour and the eyesight will change with age, people said to have normal colour vision may still have a bias to red or blue colours, thus making an impartial evaluation difficult.*

The appearance of an object with reference to colour is very subjective to the individual, what one person may describe as deep red, another person may say is crimson. One way to overcome the problem is to give colour a numeric value, there

are numerous colour space systems that are used to quantify colour such as XYZ and L*C*h, this study will use the L*a*b* colour space as it is one of the most popular used in the majority of fields. Figure 5.4 is the representation of the L*a*b* colour space (Konica-Minolta 1998).

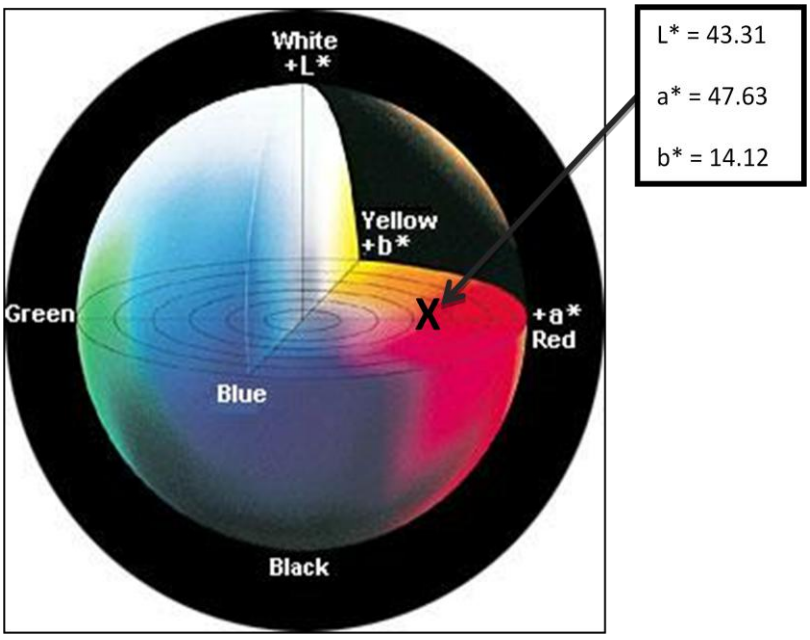


*Figure 5.4 Representation of the L*a*b* colour space. (Konica-Minolta 1998)*

The lightness of colour is represented by the L*numeric value, this will be between 0-100, with 100 being white and 0 being black. The a* numeric value range is +60 to -60, thus relating to the red and green colours, the value between 0 and +60 is the saturation of red, with +60 being the most saturated, 0 to -60 is the saturation of green, with -60 being the most saturated. The b* numeric value range is +60 to -60, thus relating to the yellow and blue colours. The value between 0 to +60 is the saturation of yellow with +60 being most saturated and a value between 0 and -60 is the saturation of blue with -60 being the most saturated.

To relate this characteristic to a particular colour, using a red apple as an example, the three values give a point on the three dimensional colour space represented in Figure 5.4. This point identifies the red apple as having a high saturation of red with a little yellow and medium lightness. Using this colour space model everyone can refer to the same colour without bias and opinion (Konica-Minolta 1998).

5.2.2 Spectrophotometry

A spectrophotometer provides high accuracy measurements of colour, the hue, lightness saturation and also gives the colour a numeric value using the L*a*b* colour space described earlier. The spectrophotometer used in this study was from Konica Minolta, model CM-2600d.

The spectrophotometer works when a beam of light from a source, strikes the object under test and deflects off the surface, the angle of light received by the detector is known as the optical geometry. This study used an integrated sphere to illuminate the test piece uniformly from all directions, the optical geometry 0/d was used, thus allowing the collection of light from all directions. Using this method the specular reflectance is excluded called the specular component excluded (SCE) function, the reflected light within +/-5 degrees from the specular angle was included. The spectral sensor has multiple sensors, each being sensitive to a particular wavelength giving a more accurate colour reading compared to the tristimuras method that has three sensors corresponding to the cones of the human eye (Konica-Minolta 1998). The microcomputer then processes the data and the numeric L*a*b* values are determined (Konica-Minolta 1998; Vaughn 2009).

5.3 Characterisation of deposit structure

The surface characterisation of the deposits used within this study was carried out using scanning electron microscopy and atomic force spectroscopy; it is by no means an in-depth evaluation but a comparison between the deposits surface. The surface of a material and how it interacts with the environment is crucial for the electroplating industry in terms of corrosion, as explained throughout Chapter 4. The surface of a solid could be said to be the layer of atoms in immediate contact with the environment, however, the atoms directly below will have a structural and chemical effect on the atoms above (Vickerman 1997). The surface is often referred to as the first 2-10 atomic layers, a depth of 0.5-3nm, although within the electroplating industry the protective layer is often in the range of 10-100 nm or in some cases thicker and this is thought of as the surface layer, but above 100 nm it is more accepted as the bulk material (Vickerman 1997).

Each deposit under test was inspected for surface characteristics consistent with the deposit and reported in this study, any isolated surface defects identified such as scratches or miss plating due to gas bubbles were disregarded. Scanning electron microscopy images shown in this study are typical of the deposit under test and not bias on current density or deposit thickness. Atomic force microscopy roughness results were taken at three areas across the panel (high medium and low current density areas) and an average value was given. The AFM image used in this study was selected from one result which showed a true image of the electroplated deposit and not bias towards current density or thickness.

5.3.1 Scanning Electron Microscopy

The scanning electron microscope (SEM) is widely used and regarded as a highly valued tool in research and industrial applications, due to the advantages it has over optical microscopes. The SEM has a large depth of field so more of the specimen is in focus at any one time, it has a much higher resolution relating to higher magnifications, often in the region of up to 300,000 times whilst giving a more three dimensional image (Attaberry 2009). This study used a Jeol instrument, model JSM-5600L V to produce surface images of the deposits plated, varying magnifications were used and are reported with each image. Numerous corrosion studies such as those carried out by Mishra et al, Wylie et al and Xu et al use the SEM as one of the techniques published in their work (Mishra 2004; Wylie 2007; Xu 2011).

The image is produced by using electrons instead of light, the electrons are produced by an electron gun and directed towards the sample, once the beam hits the sample, electrons and X-rays are ejected from the sample and are detected (Attaberry 2009). Figure 5.5 is a schematic diagram of the SEM.

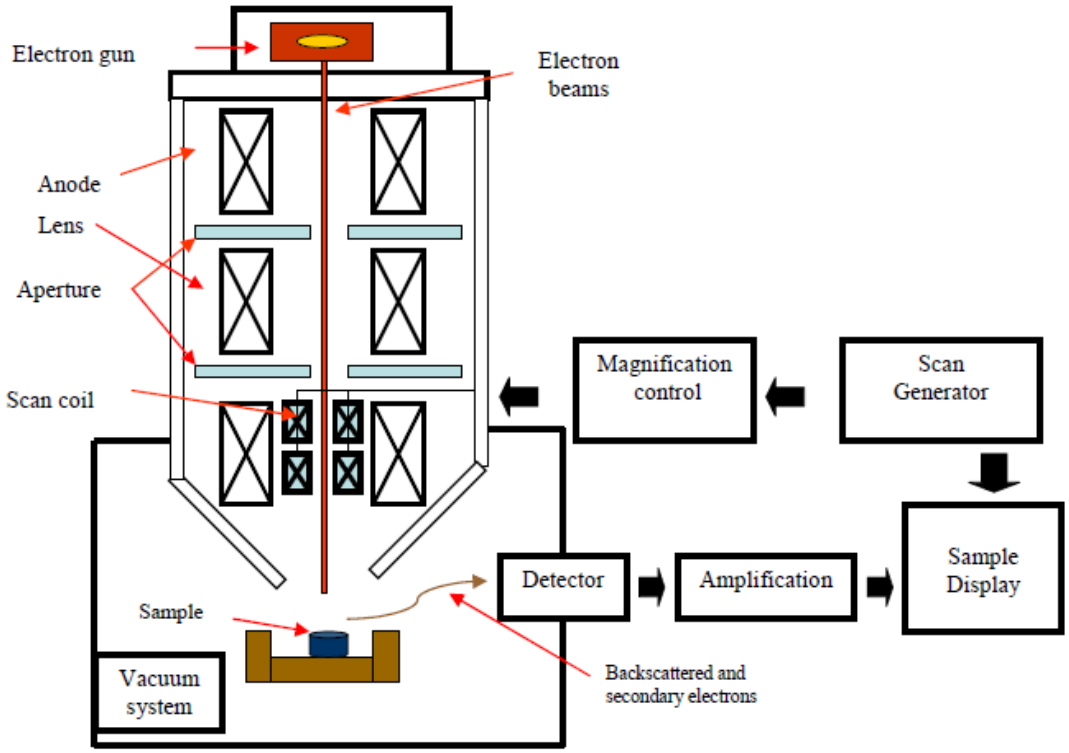


Figure 5.5 A schematic diagram of a scanning electron microscope (Lewis 1992)

The electron gun produces a steady stream of electrons, there are two types, one system uses thermionic emission from a heated filament, often a tungsten wire. Temperatures above 2700 kelvin emits plentiful amounts of light and electrons, here the electrons are accelerated across a potential difference of tens or hundreds of kilovolts, thus, generating a controlled energy of a beam of electrons that are accelerated rapidly towards the specimen through a circular hole in the microscope column. The Wehnelt cap is held at a slightly more negative voltage than the filament, thus allowing the control of the diameter area at the end of the filament. The path of the electrons usually cross and the diameter of the beam is dependent on the area of the filament, this being important for calculating the resolution of the SEM. A field emission gun offers a higher measurement of electrons per second on a given area of the specimen. This technique creates a strong electrical field to pull electrons away from the atoms they are associated with; this method is known as

tunnelling and as a result more electrons (a factor of a thousand or more), are drawn away than possible with the thermionic emission technique (Goodhew 1988).

Magnetic lenses are used to control the path of electrons, thus directing them to the specimen. This is carried out by the electrons entering the lens, the electrons experience a magnetic field and with the influence of a small force of magnitude (from the radical component), forces the electrons to travel in a helix along the lens (Goodhew 1988). The operator can control the magnification of the image by controlling the electron beam to scan a smaller area. There are different detectors used to obtain different information about the specimen, the secondary detector uses secondary electrons that escape from the specimen with energy levels below 50eV. These secondary electrons are in abundance and are the most commonly used imaging signal in scanning electron microscopy. The backscatter electrons can be used to determine the composition of the specimen; these electrons are not as abundant as secondary electrons (Goodhew 1988).

The SEM requires a vacuum to stop any interference from air particles that would hinder the electrons reaching the specimen or distort the image. The sample chamber is insulated from vibrations since the specimen must remain still to obtain clear images, it also allows movement of the specimen so the operator can achieve different angles without having to remount the specimen.

Preparation of the specimen is very important to obtain the best image possible, the surface must be free from dust and any other contaminants as this will hinder the quality of the image. The specimen surface must also be conductive to obtain a good

image, if it has a non-conducting surface it can be “gold sputtered” to give the surface a conductive layer.

The SEM does have its disadvantage, one being all images are in black and white. Technology is moving forward and the ability for SEM’s to detect energy signatures during the magnification process is being explored. This means that the colour can be assigned to the different energy signatures.

5.3.2 Atomic Force Microscopy

The atomic force microscopy (AFM) is a surface imaging technique used to evaluate a conductive or semi-conductive surface at a nanometer scale. The technique can produce a three dimensional image that can be used to characterise the roughness, depth, and particle size of the surface. Many corrosion studies used the AFM for surface imaging as demonstrated by the published work of Wang et al and Wylie et al (Wang 2004; Wylie 2007). This study used a Veeco Dimension 3100 to produce the images in conjunction with the NanoScope Analysis software for the processing of the results. Figure 5.6 shows a schematic diagram of the atomic force microscopy.

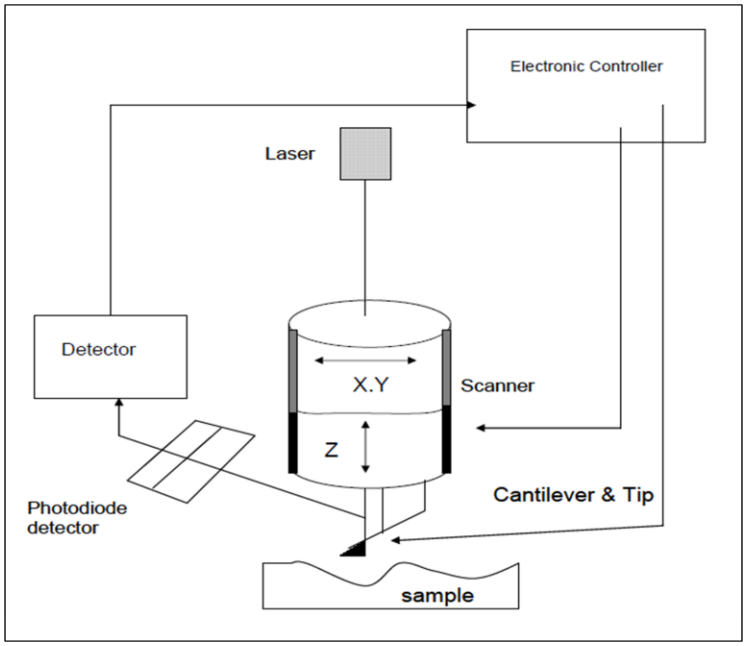


Figure 5.6 Schematic diagram of an atomic force microscopy (Triampo 2009)

The AFM works by means of a small sharp probe typically made of silicon or silicon nitride to ensure high resonant frequencies in the region of 10-100kHz and maintain a low spring constant in the region of 0.1-1Nm^{-1}. The probe is mounted on the end of a cantilever having a lateral dimension of 100µm with a thickness in the region of 1µm. As the probe is scanned over the surface the cantilever bends with the topography of the surface due to: Van Der Waals forces; electrostatic forces and magnetic forces. This deflection of the cantilever is detected by a laser beam and reflected to a photodiode or laser detector and processed by the computer. There are different operating modes used depending on the surface characteristics of the specimen (Blanchard 1996; Vickerman 1997; Triampo 2009).

Contact mode: *The tip of the probe is dragged over the surface staying in contact at all times, the cantilever vertical deflection is detected giving an indication of the samples height, thus in effect measuring the repulsion forces. A dc bias voltage is utilised to control the piezoelectric scanner (Vickerman 1997).*

Tapping mode: *The tip of the probe oscillates around 5-400kHz to the cantilever as it moves, therefore not in constant contact with the surface but it does touch the surface and then moves completely away, the laser can detect when the tip is in contact and records the movement, thus mapping out the surface (Triampo 2009).*

Non-contacting mode: *The tip of the probe has no contact with the surface but stays close to the sample at all times. The cantilever is oscillated at high frequency, close to the resonant frequency, with a large amplitude of oscillation. The probe senses long-range attractive forces and the lateral force exerted during scanning is virtually zero. As the probe is attracted by the surface this measurement is taken to draw a topographic map. This mode is often used for soft materials or weakly bound adsorbates (Vickerman 1997).*

The laser measures the magnitude of deflection which reflects at an oblique angle from the tip of the probe, a "map" of hills and valleys from the sample surface is created by plotting the laser deflection against the tip position, thus resulting in a three dimensional image and data collected can be interpreted to characterise the surface of the sample

Surface roughness is used to characterise the surface in terms of its deviation from an ideal atomically smooth surface, for example, it can be used to distinguish the pore size distribution across the surface. When roughness is calculated it generates a variety of statistics that are calculated according to each pixel in the image, this can be used in several ways (Skolnik 2000; NanoScope 2010).

Average Roughness (Ra): *This is one of the most commonly used roughness statistics; it takes the average of the absolute values of the surface height deviations measured from the mean plane. This method can give the same Ra value for two surfaces with different topographies.*

Maximum Roughness (Rmax): *This is the measurement of the maximum vertical distance between the highest and lowest data point in the image.*

Root Mean Square (RMS or Rq): *This is the root mean square average of height deviations taken from the mean image data plane; it is the simple most common method for observing any changes in the surfaces topography.*

The AFM is the preferred tool for the study of the surface morphology of the fine grained deposit, it will identify the grain structure and any defects within the deposit that may hinder the appearance or corrosion protection offered by the deposit.

5.4 Evaluation of the electroplated deposit by electrochemical testing

The evaluation of a material corroding in real time can be very time consuming, therefore electrochemical techniques are used to speed up the corrosion process, thus collating a set of data in a relatively short period of time. The principles for the electrochemical methods are to apply a potential (voltage) across an electrochemical cell, thus causing a current to flow, giving a value that corresponds to the rate of the reaction taking place. The reaction is the transfer of electrons to form ions (in this

case, the corrosion process), thus triggered by the applied potential resulting in the flow of an electric current (Tait 1994).

Each electrochemical technique was carried out three times (High, medium and low current density areas) on the same panel and a mean average was taken. This was to limit the current density effect on the results. The Nyquist and bode plots reported in this study are taken from one set of results that was characteristic of the selected deposit mean result.

5.4.1 Linear polarisation

The electrochemical technique known as linear polarisation is used in this study to calculate the corrosion rate of the electroplated deposits, thus establishing if an alternative deposit under test can match or enhance the corrosion resistance of the existing nickel deposit. The main advantage with linear polarisation is that it is a non destructive technique, and can produce results relatively quickly within a few minutes, also it can determine the open circuit potential (OCP) so further direct current measurements can be made at steady state (Tait 1994). A corrosion study by Rocchini uses this technique to obtain the corrosion rate (Rocchini 1994).

A potentiostat, EG+G Instruments, Model 263A, was used to determine the corrosion current density I_{corr}. This was carried out in 5% neutral sodium chloride solution using a Ag/AgCl reference electrode over a potential range of +/-20 mV versus open circuit potential. The equilibrium time that the 1 cm^2 surface of panel was in contact with the NaCl was varied (30 or 60 minutes). Figure 5.7 shows the

corrosion cell used for the linear polarisation and electrochemical impedance spectroscopy electrochemical testing.

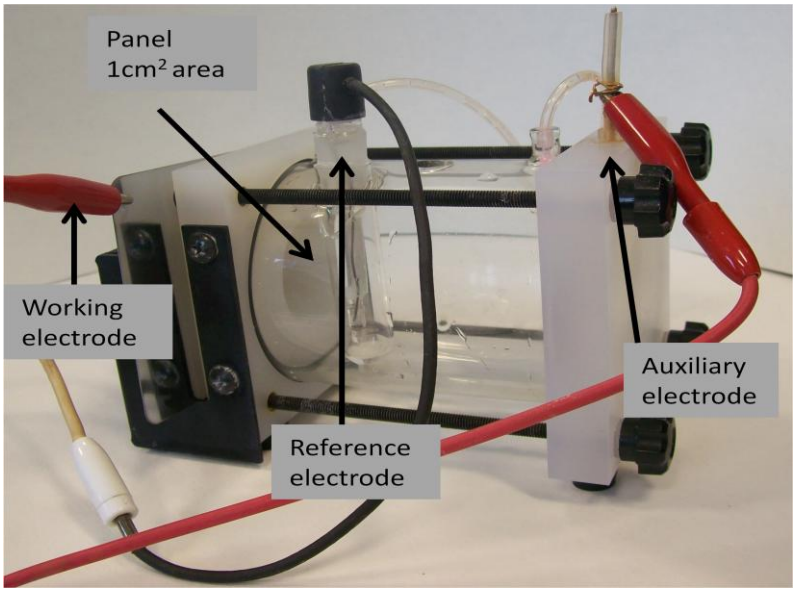


Figure 5.7 Diagram to show the corrosion cell used for both linear polarisation and electrochemical impedance spectroscopy electrochemical techniques.

The working electrode is the electroplated panel under test, 1 cm^2 area is exposed to the 5% neutral NaCl solution. The auxiliary electrode, in this case a platinum mesh provides an electric current to flow through the cell during polarisation, while the reference electrode (Ag/AgCl) provides a zero point to measure the potential difference between the working electrode and the corrosive environment.

The linear polarisation technique works by applying a voltage starting at -20mV from the OCP and ending at +20mV from the OCP, the potential is increased by 1-2mV per step and the electrical current is recorded. The data is plotted on a graph with the potential (Y axis) versus current density (X axis), this should give a straight line and therefore the polarisation resistance can be calculated from the slope of the

graph, this is demonstrated mathematically in equation 5.1. The OCP can also be read from the graph by using the data point that is recorded when the potential polarity switches from cathodic to anodic (the current density equals zero), therefore the corresponding potential is the OCP value for that deposit (Tait 1994).

$$R_p = \frac{\Delta E}{\Delta i} \tag{5.1}$$

Where

R_p = Polarisation resistance (ohms/cm^2)
ΔE = Change in potential (V)
Δi = Change in current density (Amps/cm^2)

For a practical determination on how fast the deposit corrodes and therefore making an estimate as to how long the service life will be, the data is used in equation 5.2 which demonstrates the mathematical relationship between the corrosion current and corrosion resistance (Tait 1994).

$$I_{corr} = \left[\frac{1}{2.303\ R_p}\right]\left[\frac{(\beta_a\ \beta_c)}{(\beta_a + \beta_c)}\right] \tag{5.2}$$

Where

I_{corr} = Corrosion current density (Amps/cm^2)
R_p = Corrosion resistance (ohms/cm^2)
β_a = Anodic Tafel slope
β_c = Cathodic Tafel slope
$(\beta_a\ \beta_c)/(\beta_a + \beta_c)$ is referred to as the Tafel constant.

The corrosion current can be converted to a corrosion rate in microns per year (MPY) using equation 5.3 (Tait 1994).

$$MPY = I\text{corr}\,(\Lambda)(1/\rho)(\varepsilon) \qquad (5.3)$$

Where

MPY = mils per year (1mil is equal to 0.0245mm if conversion is required)
I_{corr} = is the corrosion current density in amps/cm^2
Λ = is a combination of several conversion terms and is 1.2866x10^5
ρ = is the metal density in grams/cm^3
ε = is the equivalent weight of the metal in grams (equivalent weight is the molecular weight of the metal divided by the number of electrons in the anodic half reaction)

Equations 5.2 and 5.3 were developed by Stern and Geary, the following assumptions were made (Stern 1957; Stern 1958; Tait 1994).

1. *Both the anodic and cathodic corrosion reactions are controlled by the corrosion reaction activation energy.*
2. *Corrosion reactions for the system being measured are reversible.*
3. *Polarisation is due to corrosion.*
4. *Electrode surface changes do not occur during polarisation.*
5. *The energy barrier for the forward and reverse corrosion half equations are symmetrical.*

These assumptions do not apply to a practical situation and therefore they can only be estimates, nevertheless it can be a useful tool for comparison. Limitations to linear polarisation include, localised corrosion sites can not be identified and also the type of kinetics controlling the rate of corrosion. There can be difficulties obtaining linear data in high resistance solutions, or metals that have extremely low corrosion

rates even when this is accounted for, thus making calculations less accurate (Tait 1994).

5.4.2 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) maybe used to evaluate the corrosion resistance of a material, it is a very sensitive method and can be difficult to interpret the results (Xu 2011). A study by Orazem et al shows that the raw data obtained by EIS alone can give ambiguous results but by combining the physical and chemical characteristics of the system it is possible to get reliable restults (Orazem 2008). A study by Bostan et al uses electrochemical investigations to establish if phenothiazine derivatives improve the corrosion resistance of bronze (Bostan 2012), while a study by Jafari et al uses EIS to investigate the corrosion behaviour of metallic parts in a fuel delivery system (Jafari 2011).

Oliver Heaviside in the 1880's first introduced the concept of electrical impedance and soon after the development of vector diagrams and complex numbers were represented by A. E Kennelly and C. P Steinmetz (Lvovich 2012). Scientific advances; improvements in instrumentation; more elaborate mathematics and exposure have led to the increase in experimental applications. The development of the double-layer theory led to the development of the equivalent circuit modelling as a representation of the impedance data by Randles and Warburg (Orazem 2008). Impedance based investigation continued to develop due to: further studies of electrochemical reactions coupled with diffusion; adsorption and effects of porous surfaces on electrochemical kinetics and non-uniform current and potential distribution dispersions.

Impedance takes the phase differences between the input voltage and output current into account and therefore, is more general than simply pure resistance or capacitance. Impedance is the ratio between voltage and current, thus demonstrating the ability of a circuit to resist the flow of electrical current, represented by the "real impedance" term and the ability to store electrical energy, represented by the "imaginary impedance" term. When a current flows through a series of resistors, capacitors and inductors, this complex resistance can be defined as the impedance, this definition is applied to both direct current (DC) and alternating current (AC) (Lvovich 2012).

In experimental situations electrochemical impedance is normally measured using excitation AC voltage signal with small amplitude applied at a frequency. The voltage signal expressed as a function of time has the form as shown in equation 5.4. In this notion a "radical frequency" (ω) of the applied voltage signal parameter is introduced, which is related to the applied AC frequency as $\omega = 2\pi f$ (Lvovich 2012).

$$V(t) = V_A \sin(2\pi f t) = V_A \sin(\omega t) \qquad (5.4)$$

Where

V(t) = Voltage expressed as time
V_A = Small amplitude (volts)
t = time (seconds)
f = frequency (Hz)
ω = radical frequency (radians/second)

EIS works on the principle that if the applied potential is sinusoid then the current will be sinusoidal and therefore the current will flow. The EIS voltages cycle from

anodic to cathodic magnitudes and vice versa using a spectrum of AC voltage frequencies. From each frequency the capacitance and resistance of the circuit can be obtained, thus providing the relevant data for corrosion behaviour and corrosion rates (Tait 1994).

AC current and voltage have both magnitude and direction and therefore are vectors, this is also the same for impedance as it is measured as a function of AC voltage and current. The total impedance magnitude is shown mathematically in equation 5.5, based on the simple equivalent circuit shown in Figure 5.4 (Tait 1994).

$$Z = R_1 + \frac{R_2}{1+(\omega R_2 C)^2} + \frac{j\left[-\omega {R_2}^2 C\right]}{1+(\omega R_2 C)^2} \qquad (5.5)$$

Where

Z	= total impedance in ohms
R_1/ R_2	= resisters within the circuit in figure 5.4
C	= capacitor capacitance in Farads
ω	= 2π (AC voltage frequency)
j	= is the square root of -1 and is referred to as an imaginary number

The magnitude of the X-component vector is equal to the second term in equation 5.5, which is $\frac{R_2}{1+(\omega R_2 C)^2}$ and is referred to as the real impedance, where Y-component vector is equal to the third term in equation 5.5, which is $\frac{j\left[-\omega {R_2}^2 C\right]}{1+(\omega R_2 C)^2}$ and is referred to as imaginary impedance. Equation 5.5 demonstrates that each polarising voltage frequency produces a different magnitude for phase angle, total impedance and the component vectors (Tait 1994).

This study used the Solartron 1252A frequency response analyser with the Princeton Applied Research Potentiostat/Galvanostat, Model 263A, and ZPlot software. This

was carried out in 5% neutral sodium chloride solution using a Ag/AgCl reference electrode. The equilibrium time that the 1 cm^2 surface of panel was in contact with the NaCl was varied from 30 to 60 minutes.

The electrochemical cell can be represented by a series of resistors and capacitors known as an equivalent circuit, Figure 5.8 demonstrates a simple equivalent circuit with one time constant, the equivalent circuit can be interpreted from the impedance spectrum and then determine the significance of each component. A capacitor is used to store electric charge but it takes time for it to become fully charged, it is this difference in time that alters the current and amplitude curves referred to as the phase angle, the magnitude of the phase angle is different for each polarising voltage frequency. A resistor will resist the passage of an electric current but will not accumulate and separate charge when polarised by an AC voltage, it also doesn't exhibit time behaviour or frequency dependency during polarisation and when the phase angle is zero (Tait 1994; Cogger 1999).

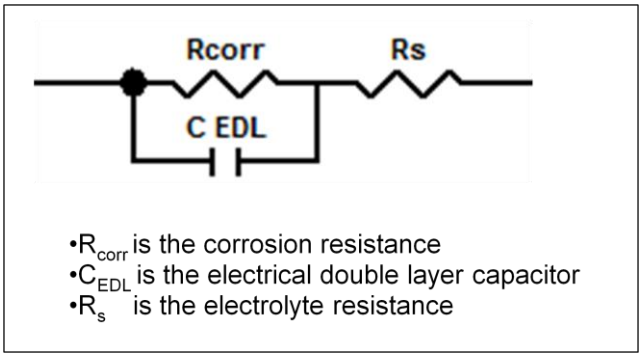


Figure 5.8 A simple equivalent circuit with an electrical behaviour of an electrical double layer.(Tait 1994)

AC voltages cause ions to move to and from the counter and working electrodes in response to the changing voltage magnitude and polarity; Figure 5.9 shows a corroding metal electrical double layer (EDL) and the corresponding electrical circuit. The electrical circuit in Figure 5.9 shows the metal corrosion resistance (R_{corr}), uncompensated solution resistance (R_s) and the EDL capacitive reactance (C_{EDL}) (Tait 1994).

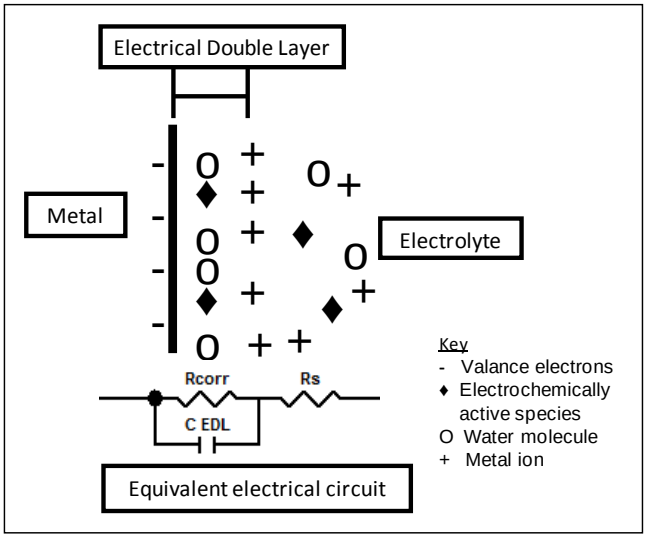


Figure 5.9 A corroding metal electrical double layer and the corresponding electrical circuit.(Tait 1994)

There are several ways to plot EIS data, the most common types of EIS graphs are

- Complex plane plot (Nyquist plot)
- Bode magnitude
- Bode phase plot

The Nyquist plot uses the real and imaginary impedance (which is expressed as a complex number), the real impedance is plotted on the X-axis with high frequency data on the right and low frequency data on the left, the imaginary impedance is

plotted on the Y-axis often as a negative value, Figure 5.10 shows the Nyquist plot to the equivalent circuit in Figure 5.8. Figure 5.10 shows a semicircle, typical of a single "time constant", more complex circuits show several time constants and can be represented as a partial semicircle (Gramry-Instruments 2007).

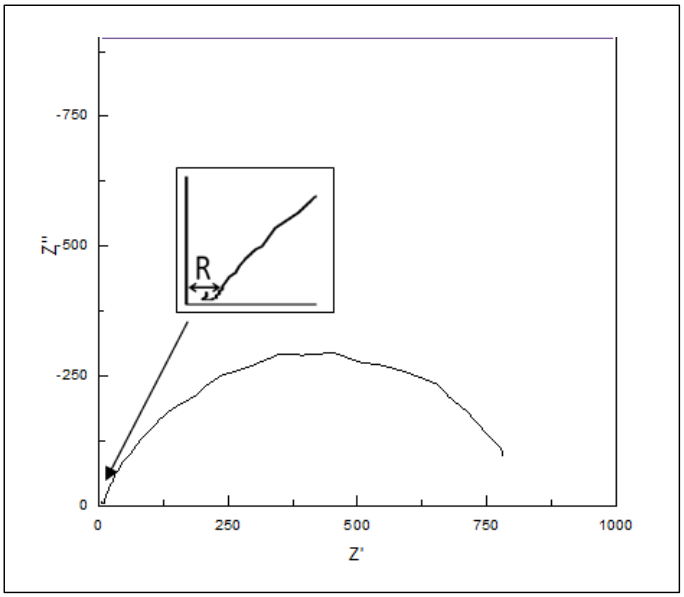


Figure 5.10 Example of a Nyquist plot of a simple circuit

The Bode plot (Figure 5.11), shows the impedance plotted with log frequency on the X-axis and both the absolute values of the impedance and the phase-shift on the Y-axis, it also shows the frequency of each data point unlike the Nyquist plot (Gramry-Instruments 2007).

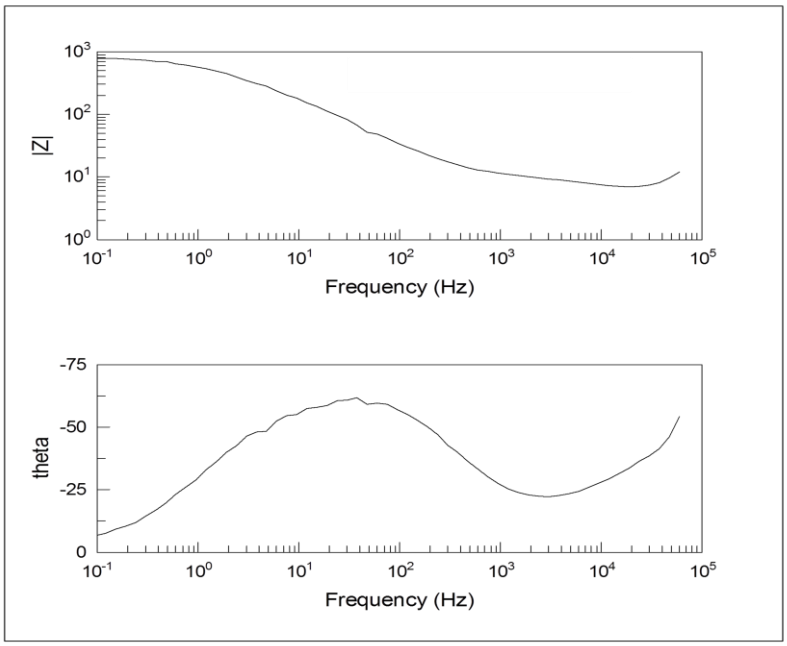


Figure 5.11 An example of a Bode plot from a simple circuit

Electrochemical cells are not linear, if the input voltage is doubled the output current is not necessarily doubled, but it is easier to interpret a linear system and so taking a small section of the current versus voltage curve it appears to be linear, also known as pseudo-linear. To maintain the pseudo-linear system a small 1-10mV AC signal is applied to the cell. It is also important to maintain a steady state, since if the system shifts, inaccurate results are generated. In practice it can be difficult to maintain a steady state due to numerous changes that take place during the reaction, these include the formation of an oxide layer, contamination or build up of reaction product (Tait 1994).

Solution resistance is often a factor in the impedance of an electrochemical cell, the solution resistance between the reference and working electrode must be considered when interpreting the result, a three way potentiostat will compensate for the solution resistance between the reference and counter electrode. On the Nyquist plot

the solution resistance can be seen on the X-axis before the semicircle, this is denoted as R in Figure 5.10 (Tait 1994).

Double layer capacitance results from charge separation at the interface between the electrode and the electrolyte, this is a very small distance and often in the order of angstroms in thickness. The charged electrode is separated from the charged ions and therefore forms a capacitor, the value of the double layer will depend on a number of factors including, temperature, electrode roughness and an oxide layer (Tait 1994).

5.5 Evaluation of corrosion resistance of a deposit using accelerated salt spray test

Corrosion resistance of a deposit is important to manufacturers and consumers as it will determine the level of corrosion protection and the life of the product. For instance, in the automotive industry, the car logo must be corrosion resistant for years to maintain the look of the vehicle. Since the test will be time consuming to allow the atmosphere to corrode the parts, accelerated corrosion tests have been developed to reduce the testing times. There are numerous tests used but within the electroplating industry the common ones include, Neutral Salt Spray (NSS) and Copper Accelerated Acetic acid Salt Spray (CASS) (Altmayer 1999).

Specifications are used throughout this study and are an important part of the electroplating industry. A specification is defined by Lowenheim (Lowenheim 1978)as follows;

"A concise statement of a set of requirements to be satisfied by a product, material or process indicating, whenever appropriate, the procedure by which it may be determined whether the requirements are satisfied. As far as possible, it is desirable that the requirements be expressed numerically in terms of appropriate units together with their limits."

The use of specifications allows the manufactures, purchasers and customers a consistency in quality and comparison within the industry (Lowenheim 1978; Altmayer 1999; Singleton 2012). It also allows an accurate comparison of the deposits used within this study to be reliable and consistent.

For both the NSS and CASS the equipment, handling and specification for evaluation of the test specimens are the same, the difference is the salt solution and operating conditions which are outlined in section 5.5.1 and 5.5.2 (ASTM 2009; ASTM 2009).

The apparatus required to carry out these tests must contain a fog chamber with a provision for heating, salt reservoir, supply of compressed air, at least one atomising nozzle, specimen support, and means of control. All equipment used must be corrosion resistant to the fog and not affect the corrosiveness of the fog (ASTM 2007; Singleton 2012).

The metallic test specimen must be clear of any dirt, dust or oil unless otherwise agreed as this can influence the corrosion resistance of the deposit. To clean the sample, 10 grams of magnesium oxide powder in 100 millilitres of distilled water

can be used to wipe over the sample's surface with cotton wool and rinsed under warm water before drying. As a precautionary measure any cut edges or jig points must be masked off with either pressure sensitive tape, stopping off lacquer or wax, thus avoiding localised corrosion on the non protected areas (ASTM 2007).

The positioning of the test specimen is important in order to expose the test area, support or suspend the specimen at a 15^{o} parallel to the principal direction of horizontal flow of fog through the chamber, based on the dominant surface under test. The test specimens must not touch each other or be in contact with any other metal or positioned in a way to stop the salt solution collecting on the test surface and thereby drip onto other test specimens (ASTM 2007).

Each chamber must contain at least two fog collectors in the proximity of the test specimens, one close to a nozzle and the second farthest away from the nozzle. This is used to evaluate the collection rate and can be used to analyse the salt concentration and pH (ASTM 2007).

For both the NSS and CASS tests, three panels of each electroplated deposit under test was used and a mean average was taken for the corrosion rating following the ASTM 537-70 specification, this was to eliminate any isolated imperfections on the surface that were not characteristic of the electroplated deposit (ASTM 2007). The electroplated panels under test were prepared following the ASTM 537-70 specification, the panels did not require cleaning as they were wrapped in acid free paper after electroplating to stop any dirt or dust settling on the surface, the edges of each panel were taped to stop localised corrosion from the jig points and all panels

were positions as required by the specification (ASTM 2007). An accelerated corrosion study by Papadopoulos et al (2007) uses the salt spray test following the ASTM specifications (Papadopoulos 2007).

5.5.1 Neutral salt spray

The standard test method for neutral salt spray (NSS) follows the specification ASTM B 117-07 (ASTM 2009), this study used an Ascot corrosion cabinet. The test method is not limited to the type of finish and does not detail the type of test piece or exposure time, nor the interpretation of the results. The test was designed to provide a controlled corrosive environment which can produce corrosion resistance results for metals and metal plated parts, this is a widely accepted test method used in the electroplating industry for all different finishes. Table 5.9 outlines the operating conditions for NSS testing (ASTM 2009).

Conditions		**Parameters**
Salt solution	Water	Make up to 1 litre
	Sodium Chloride	45-55g/l
	pH (adjust with dilute hydrochloric acid or sodium hydroxide.)	6.5-7.2
Air pressure		83-124 kPa
Humidifier temperature		46-49^{o}C
Chamber temperature		33-37^{o}C
Collection rate		1-2 ml/hour
SG of collection		1.0255-1.0400

Table 5.9 Operating conditions for NSS testing (ASTM 2009)

5.5.2 Copper accelerated acetic acid salt spray

The standard test method used for copper accelerated acetic acid salt spray (CASS) testing is ASTM B 368-97 (ASTM 2009). This study used a Liebisch, model 33649 corrosion cabinet. This specification describes the conditions required to undertake CASS testing, this method is used to evaluate the performance of the decorative process copper/nickel/chromium, or nickel/chromium on the substrates, steel, zinc alloys, aluminium alloys and plastics designed for severe service. NSS proved to be a slow process to corrode the nickel/chromium deposit and therefore a more severe test was required to reduce the testing time. CASS was developed to accommodate this problem and proved to work well, and as a result it has become an established method for the electroplating industry. Table 5.10 outlines the operating conditions for CASS testing (ASTM 2009).

Conditions		**Parameters**
Salt solution	Water	Make up to 1 litre
	Sodium Chloride	45-55g/l
	Copper Chloride	0.25g/l
	pH (adjust with glacial acetic acid)	3.1-3.3
Air pressure		0.08-0.12Mpa
Humidifier temperature		60-65^{o}C
Chamber temperature		48-51^{o}C
Collection rate		1.0-2.0 ml/hour
SG of collection		1.030-1.040

Table 5.10 Operating conditions for CASS testing (ASTM 2009)

5.5.3 Evaluating the test specimen

Evaluating the test specimens is by visual examination and guided by the specification ASTM B 537-70 (ASTM 2007). This specification is intended for use with natural atmospheric test sites and accelerated corrosion tests using the specification ASTM B 117 and ASTM B 368. It is for the evaluation of copper/nickel/chromium and nickel/chromium deposits that are cathodic to the substrate and used in a decorative application (ASTM 2007).

This specification uses two ratings, the first referring to the appearance of the substrate corrosion also known as the protection number or rating, the second referring to the appearance of the coating itself and referred to as the appearance number or rating. To describe the type and severity of any defects agreed symbols and abbreviations can be used (ASTM 2007).

Predictions on how the finish will perform out in the natural environment compared to the results from the NSS or CASS cannot be correlated but it can be compared to other finishes that have undergone the NSS or CASS test following the same specification. Small variations may occur due to different chambers, test pieces and the subjective evaluation, therefore multiple test samples should be evaluated to minimise these errors (ASTM 2007).

5.6 Procedures for electrodeposition onto a substrate

Brass panels (size 10 × 7.5 × 0.05 cm) were used as the substrate for all experiments carried out in this study. The pre-treatment process remained consistent throughout

the study as described in section 5.1.1. Figure 5.12 shows the electroplating sequence for the deposition of nickel and chromium. These panels were used as a bench mark for all other deposits during this study. The nickel was plated to a thickness of 20µm followed by 0.3µm of chromium if required. The formulations and electroplating conditions for the nickel and chromium deposits are outlined in sections 5.1.2 and 5.1.3 respectively.

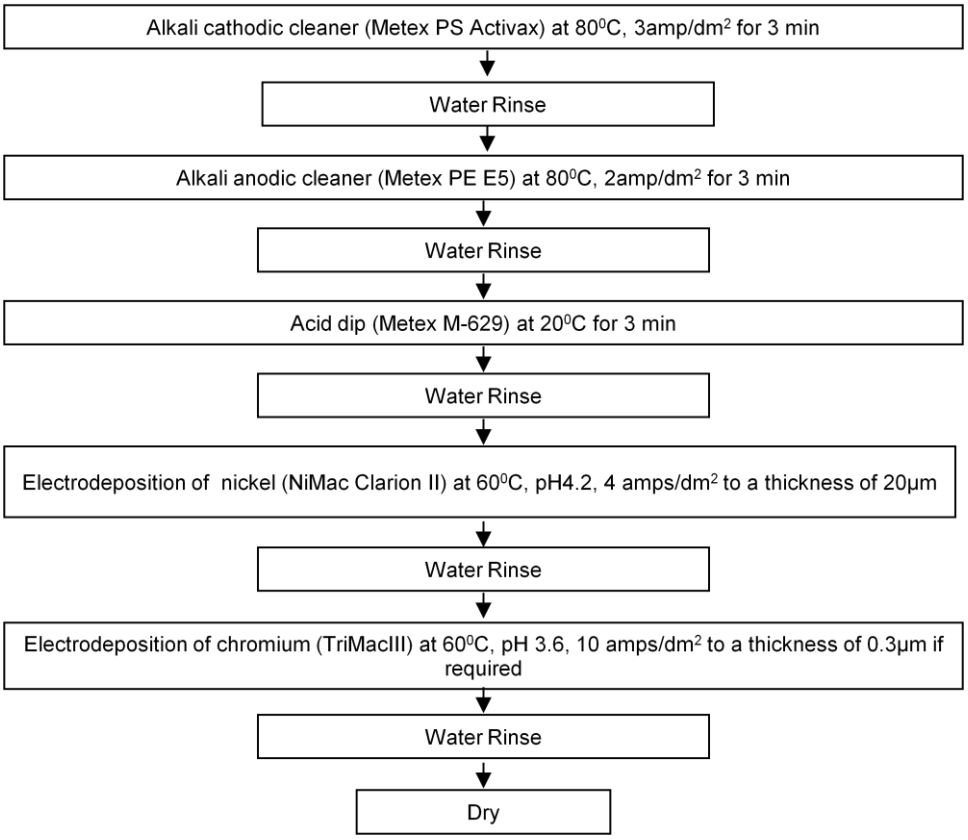


Figure 5.12. Process sequence for the electrodeposition of nickel deposit and trivalent chromium onto a brass substrate.

The electroplating sequence for the alternative deposit white Cu-Sn alloy is outlined in Figure 5.13. After the pre-treatment stage, copper was electrodeposited to a thickness of 20µm, followed by the white Cu-Sn alloy at varying thicknesses of either 0.5µm or 2µm, the chromium was then deposited to a thickness of 0.3µm if

required. All the operating conditions for the deposition of copper and white Cu-Sn alloy are described in section 5.1.4 and 5.1.6 respectively.

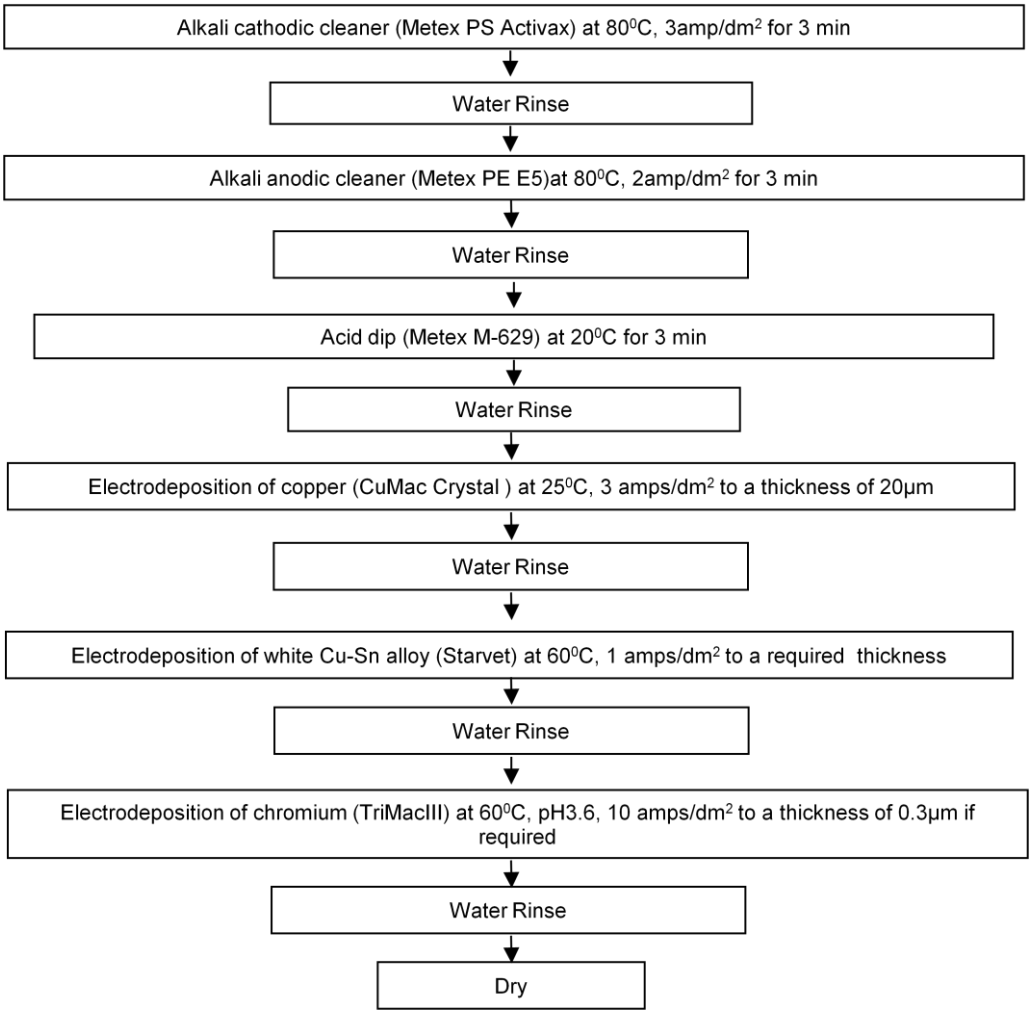


Figure 5.13 Process sequence for the electrodeposition of white Cu-Sn deposit and trivalent chromium onto a brass substrate.

The electrodeposition sequence for yellow Cu-Sn alloy is shown in figure 5.14, after the pre-treatment sequence copper was electrodeposited to a thickness of 20µm, followed by the electrodeposition of the yellow Cu-Sn alloy plated to either 4µm, 12µm or 24µm, followed by 0.5µm of electrodeposited white Cu-Sn alloy if required, then 0.3µm of chromium if required. The formulation and operating parameters for the yellow Cu-Sn alloy is described in section 5.1.5.

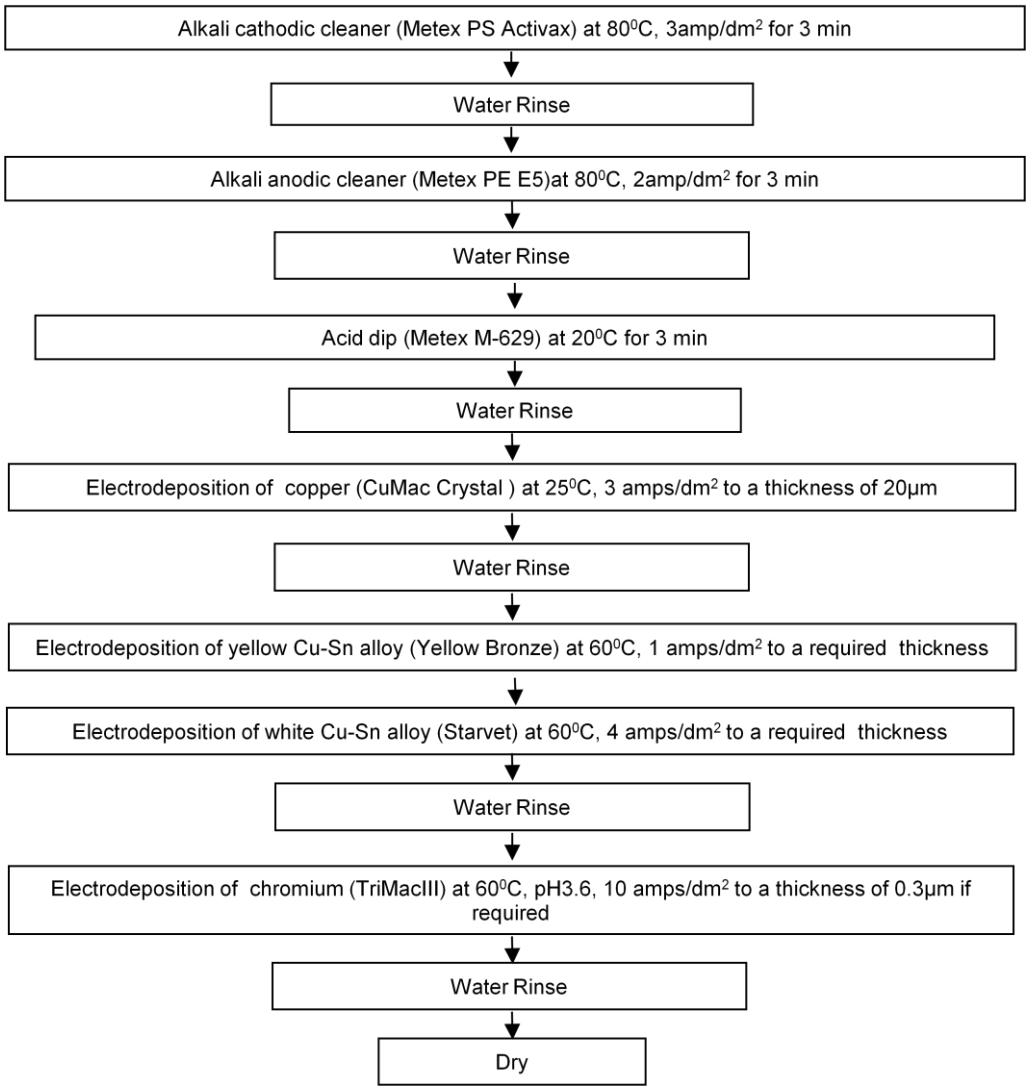


Figure 5.14 Plating sequence for the electrodeposition of yellow Cu-Sn deposit followed by white Cu-Sn deposit and trivalent chromium onto a brass substrate.

The white Cu-Sn alloy deposit is not plated commercially above a few microns due to its change in appearance from a silvery bright deposit to a dull grey deposit (which is unsuitable as a nickel replacement), therefore the copper was plated to give the same overall deposit thickness as the standard nickel deposit. This approach allowed the corrosion testing to be comparable between the two plating sequences as a similar overall deposit thickness was achieved. When evaluating the yellow Cu-Sn alloy in combination with the white Cu-Sn alloy it was determined that the white Cu-

Sn alloy would provide the appearance and therefore only a thin deposit was required.

The plated panels were subjected to appearance testing using a spectrophotometer to provide the L*a*b* colour space values (section 5.2.1), the deposits structure were determined by the scanning electron microscope (section 5.3.1) and the atomic force microscope (section 5.3.2). The corrosion resistance of each deposit was assessed electrochemically by linear polarisation (section 5.4.1) and electrochemical impedance spectroscopy (section 5.4.2) and also by accelerated salt spray testing using neutral salt spray (section 5.5.1) and copper accelerated acetic acid salt spray (section 5.5.2). All the results are reported in chapter 6.

The panels once plated underwent investigations to determine their corrosion resistance, appearance and deposit structure. Varying deposit thicknesses where evaluated to identify any advantages and disadvantages for each potential alternative, all plating thicknesses will be outlined with the results in chapter 6.

Summary

Chapter 5 described the methodology and experimentation for this study to assess the appearance, structure and corrosion resistance of the existing nickel/chromium process and also for any plausible alternative replacements for nickel deposit. The individual deposits were investigated separately and also as a combined sequence to identify all aspects of the plating process.

CHAPTER 6: RESULTS AND DISCUSSION

Introduction

This chapter documents the results obtained in this study for all the techniques used to electroplate and evaluate each electroplated deposit. The appearance of the deposits have been compared by a spectrophotometer using the L*a*b* colour space and the topography of the deposit will be identified by using both the scanning electron microscope and the atomic force microscope. Results from the electrochemical techniques, linear polarisation and electrochemical impedance spectroscopy identified the corrosion resistance of each electroplated deposit, while the accelerated corrosion tests using both neutral salt spray and copper accelerated acetic acid salt spray were used to evaluate the corrosion resistance by assigning a corrosion rating to each electroplated deposit throughout the duration of the test.

Factors such as longevity, quality, value and sufficient corrosion resistance are important when alternatives are being evaluated so as to maintain the quality of the new products, and also to be compatible with existing nickel and chromium. This chapter will therefore critically analyse the results collected in this study to determine if an alternative deposit could be a suitable replacement to nickel under decorative trivalent chromium.

6.1 Spectrophotometry results

A spectrophotometer was used to accurately measure the colour of each electroplated deposit using the L*a*b* colour space, the mean average of three readings were taken across each panel to eliminate high and low current density colour changes. All results are presented in Table 6.1. A study by Vaughn et al demonstrated that the spectrophotometry method using the L*a*b* colour space was a more accurate technique than using digital imaging, the sampling method used in the study was to take numerous readings across the sample and calculate the mean average, the same sampling method was used in this study as explained in section 6.2 (Vaughn 2009).

Panel identification	**L***	**a***	**b***
Nickel 20µm	83.12	0.81	6.68
Nickel 20µm + Chromium	82.78	-0.21	0.66
White Cu-Sn alloy 0.5µm	86.26	0.40	3.25
White Cu-Sn alloy 2.0µm	85.86	0.44	3.33
White Cu-Sn alloy 0.5µm + chromium	82.89	-0.26	0.93
White Cu-Sn alloy 2.0µm + chromium	83.04	-0.28	0.75
Yellow Cu-Sn alloy 4.0µm	71.07	11.84	21.94
Yellow Cu-Sn alloy 12.0µm	67.12	13.50	23.88
Yellow Cu-Sn alloy 24.0µm	68.37	11.59	22.31
Yellow Cu-Sn alloy 4.0µm + chromium	78.52	-0.21	2.21
Yellow Cu-Sn alloy 12.0µm + chromium	75.35	-0.27	2.07
Yellow Cu-Sn alloy 24.0µm + chromium	77.89	-0.33	1.68

*Table 6.1 L*a*b* colour space for all electroplated deposits*

The nickel and chromium electroplating process provides a standard finish that can be identified in numerous applications by the consumer, and it is often referred to as a chromium finish. This study evaluates the appearance of the deposit using a spectrophotometer to identify the L*a*b* colour space, thus giving a numeric value to colour.

The results shown in Table 6.1 indicate that the visual appearance of the nickel deposit is bright and silver in colour, the spectrophotometer identifies it as a light deposit, with a hue verging on red and yellow, thus giving it a slight brown appearance. The chromium deposit has a similar visual appearance to the nickel, the spectrophotometer identifies the lightness of the deposit to be similar with a slight difference in the hue, meaning the chromium has a bluer appearance in comparison to the nickel.

The white Cu-Sn alloy plated to a thickness of 0.5µm is visually similar to the nickel deposit. The spectrophotometer identifies it as being lighter than the nickel with the hue being slightly yellow and red, thus again giving it a brown appearance but to a lesser extent than the nickel. The chromium finish on the 0.5µm white Cu-Sn alloy appears to darken the deposit giving it more of a blue hue, similar to the chromium on nickel, thus suggesting that it is a potential alternative to the nickel deposit in terms of appearance.

The 2.0µm white Cu-Sn alloy does not change significantly compared to the thinner 0.5µm white Cu-Sn alloy deposit remaining the same when chromium is plated on top. The visual appearance of the 2.0µm white Cu-Sn alloy shows a background haze that is not seen in the 0.5µm white Cu-Sn alloy or the nickel deposit and therefore could hinder the overall appearance of the finish and consequently could not be a suitable alternative to the nickel deposit.

The yellow Cu-Sn alloy is visually different to the other deposits and appears darker and orange in colour. The spectrophotometer identifies the deposit as being darker

(regardless of plating thickness) and having a significantly more yellow and red hue compared to the nickel. Chromium plated on top significantly brightens the 4µm, 12µm and 24µm yellow Cu-Sn alloy deposit and changes the hue, thus becoming greener and less yellow. This is still different from the chromium on nickel deposit since it is not as light and also not as blue. What is not identified by the spectrophotometer is the reflectance or gloss nature of the deposit. Visually, the 4µm, 12µm and 24µm yellow Cu-Sn alloy deposits are dull and even when chromium is plated on top it still appears dull. Overall the yellow Cu-Sn alloy with chromium deposit would not replace the nickel with chromium deposit without addressing the issue of reflectivity of the deposit.

6.2 Surface topography results

6.2.1. Scanning electron microscopy results

The scanning electron microscope (SEM) was used to identify the surface characteristics of each electroplated deposit in terms of pitting and other surface defects characteristic of the deposit. A study by Xu et al used the SEM to analyse the surface morphology and composition of electroplated deposits, the results were used as a comparison between surfaces and with other techniques the study produced results identifying the hydrophobic properties and corrosion resistance of the deposits.

The SEM images of the electroplated nickel deposit with and without the chromium are shown in Figures 6.1, 6.2 and 6.3. The nickel deposit without chromium was plated to a thickness of 20µm to minimise porosity. Figure 6.1 shows the image with

consistent and uniform small nodulations with no indication of pits or other surface defects. The chromium is plated to a thickness of 0.3µm and appears to smooth out the nodulations identified in the nickel deposit with no defects visible over the surface.

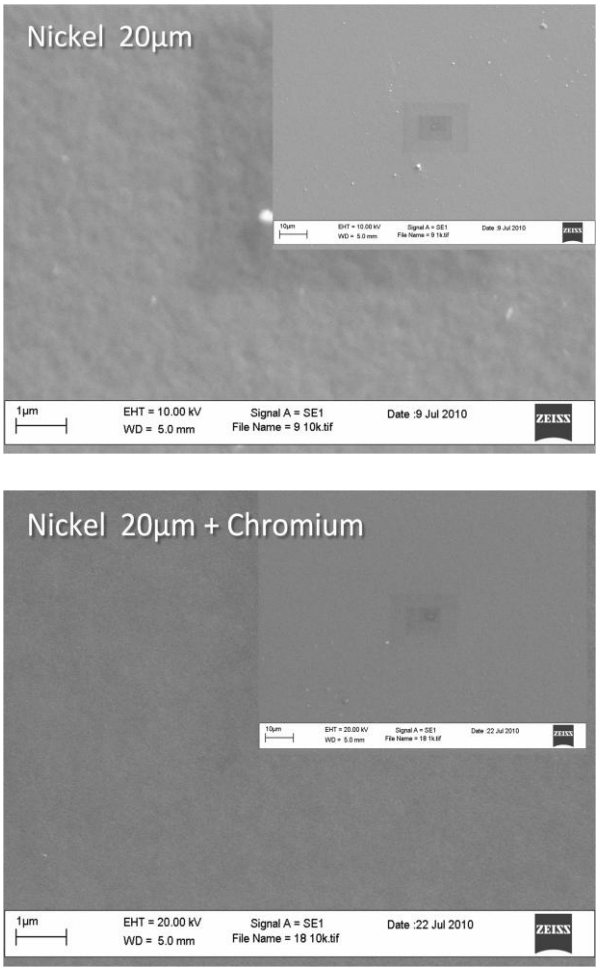


Figure 6.1 SEM images of the nickel deposit with and without chromium deposit as a topcoat.

Figure 6.2 and 6.3 show the SEM images of the white Cu-Sn alloy deposits with and without chromium and the yellow Cu-Sn alloy deposit with and without the chromium respectively.

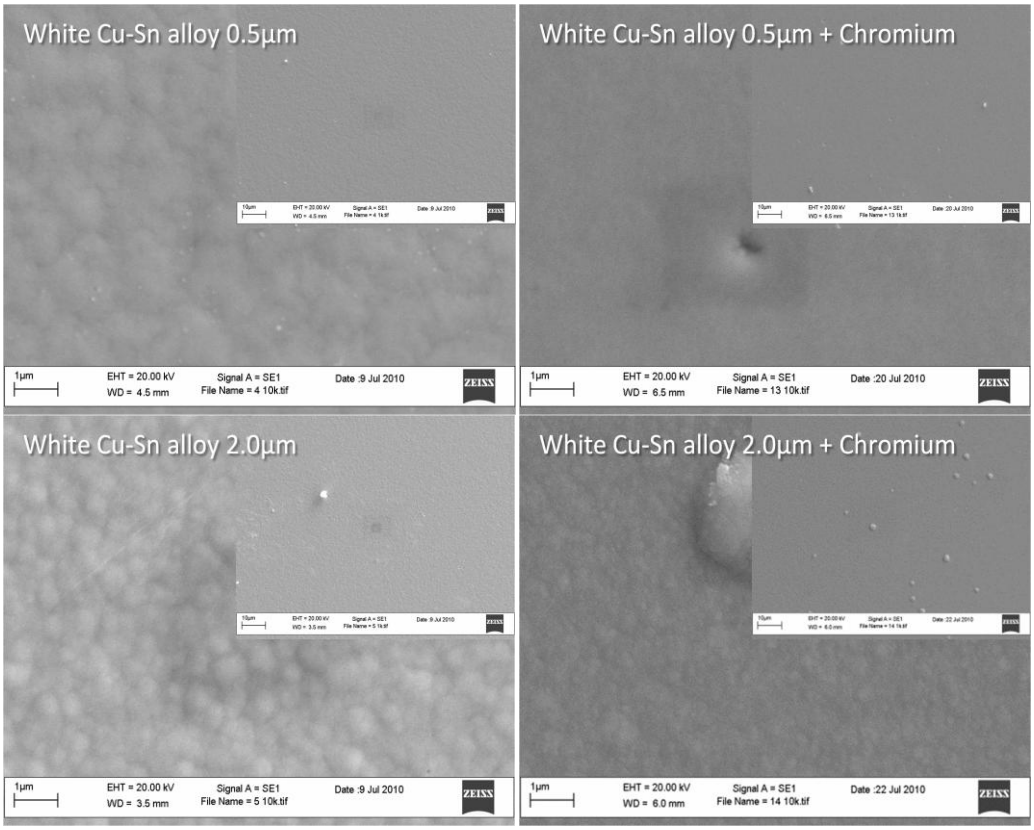


Figure 6.2 SEM images of the white Cu-Sn alloy with and without chromium deposit as a topcoat.

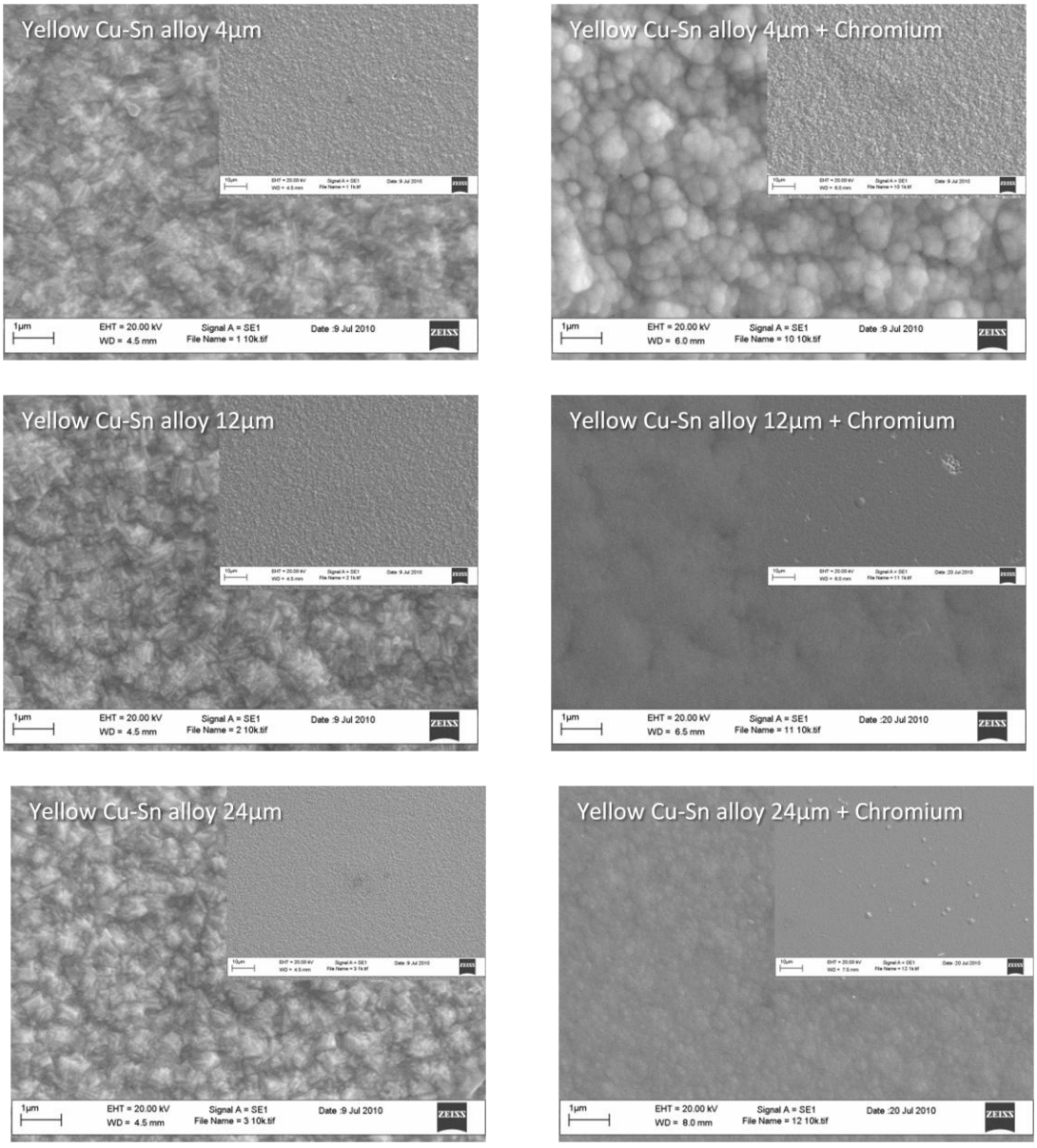


Figure 6.3 SEM images of the yellow Cu-Sn alloy with and without chromium deposit as a topcoat.

The SEM image of the 0.5µm white Cu-Sn alloy can be seen in Figure 6.2, the topography appears consistent with uniform nodules that are larger than the ones identified with the nickel deposit although no visible pores can be seen. Areas around the nodules can form trenches that are possible sites for corrosion to start, therefore, although no pores can be identified this imperfection could still hinder the corrosion resistance of the deposit. The white Cu-Sn alloy formulation does not have the same additive system as the nickel since it relies on the bright copper deposit

underneath to provide the levelling and brightness. This could be a possible explanation for the larger nodules seen in the deposit. The chromium deposit appears to reduce the size of the nodules seen on the 0.5µm white Cu-Sn alloy deposit. An imperfection or pit can be seen in the chromium deposit, and with further inspection of the chromium surface it was concluded that the imperfection identified was not seen elsewhere on the surface, and therefore would not impact the overall corrosion resistance of the deposit. The SEM image of the 0.5µm white Cu-Sn alloy with chromium deposit is similar to the nickel and chromium deposit, thus suggesting a similar deposit structure.

The SEM image of the 2.0µm white Cu-Sn alloy in Figure 6.2 shows the topography with a more defined nodulated deposit which could reduce the corrosion resistance by providing numerous sites for corrosion to start. The chromium deposit has reduced the appearance of the nodules, although it does not appear to completely smooth the deposit like the standard nickel and chromium deposit. The chromium deposit appears to have its own nodules that are sparsely spread over the panel and much larger than the ones identified with the 0.5µm and 2µm white Cu-Sn alloy deposit. This is not characteristic of the chromium deposit as it was not identified on the nickel and chromium image, therefore it could be due to the underlying 2.0µm white Cu-Sn alloy deposit.

SEM images of the 4µm, 12µm and 24µm yellow Cu-Sn alloy deposit shown in Figure 6.3 presents an uneven crystalline structure as opposed to the spherical nodules of the nickel deposit, the thickness of the yellow Cu-Sn alloy does not significantly change the structure. Electroplating chromium on top does smooth out

the crystalline structure of all the yellow Cu-Sn alloy deposits, but the 12µm and 24µm yellow Cu-Sn alloy deposits show the chromium to have its own nodules sparsely spread over the panel as seen with the 2µm white Cu-Sn alloy deposit.

Figure 6.4 shows the SEM image of the electroplated copper used under the white or yellow Cu-Sn alloy deposits.

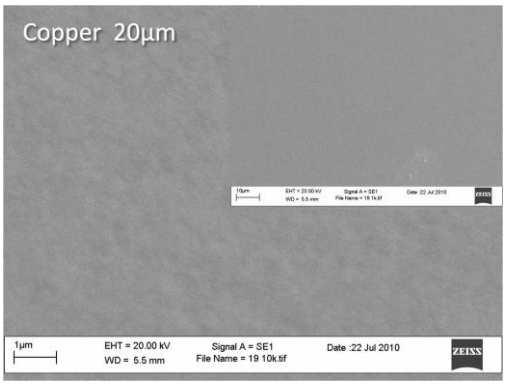


Figure 6.4 SEM images of the copper deposit.

To appreciate the influence of copper over the structure of the white and yellow Cu-Sn alloy deposits, a SEM image of 20µm of copper was analysed and shown in Figure 6.4. The image appears to be similar to the nickel deposit, thus indicating the structure seen for all the white and yellow Cu-Sn alloy deposits are not influenced by the structure of the underlying copper deposit.

6.2.2. Atomic force microscopy results

The atomic force microscope (AFM) was used to demonstrate the surface topography of each electroplated deposit and calculate the RMS (root mean square, average height deviations), Ra (average roughness) and Rmax (maximum roughness between the lowest and highest points). A study by Radlein et al uses the AFM to

calculate the root mean square (RMS) of glass to identify any surface defects and overall changes to the surface topography after treatment, this study also uses the RMS and Rmax as a tool to characterise the deposits surface (Radlein 1997).

The AFM was carried out as a continuation of the investigation into the topography of the electroplated deposits. The data presented as the Ra value is the absolute value of the surface height deviation, which could be the same for two different topographies and therefore would not help to identify any differences between the deposits. It is therefore not necessary to discuss the results related to the Ra value since they will not provide any useful information.

Table 6.2 shows all the roughness measurements, where Figures 6.5, 6.6 and 6.7 show the AFM images of the electroplated nickel with and without chromium, the white Cu-Sn alloy deposit with and without chromium and the yellow Cu-Sn alloy deposit with and without chromium respectively. Figure 6.8 shows the copper deposit used underneath the white and yellow Cu-Sn alloy deposits.

Panel identification	RMS (nm)	Ra (nm)	Rmax (nm)
Nickel 20µm	3.08	2.46	18.6
Nickel 20µm + Chromium	3.91	3.1	36.6
White Cu-Sn alloy 0.5µm	8.3	6.63	73
White Cu-Sn alloy 2.0µm	12	9.42	166
White Cu-Sn alloy 0.5µm + chromium	5.61	4.48	33.7
White Cu-Sn alloy 2.0µm + chromium	9.84	7.84	80
Yellow Cu-Sn alloy 4.0µm	41.2	33.6	276
Yellow Cu-Sn alloy 12.0µm	71.4	57.9	452
Yellow Cu-Sn alloy 24.0µm	60.8	49.5	408
Yellow Cu-Sn alloy 4.0µm + chromium	22.9	18.4	150
Yellow Cu-Sn alloy 12.0µm + chromium	66.4	53.1	464
Yellow Cu-Sn alloy 24.0µm + chromium	107	84.4	639
Copper 20µm	5.92	4.69	58.5

Table 6.2 AFM roughness results for all electroplated deposits

The nickel deposit has the visual appearance of being bright and reflective, thus indicating it is a relatively smooth finish and can be seen in Figure 6.5. The Rmax value of 18.6nm supports the smooth finish of the nickel deposit by the small distance between the maximum and minimum points, the RMS value of 3.08nm also indicates little height deviation across the deposit. Chromium as the topcoat has an Rmax value of 36.6nm with RMS value of 3.91nm, the chromium is still a visually bright and reflective finish but with increased roughness in the topography compared to the nickel deposit.

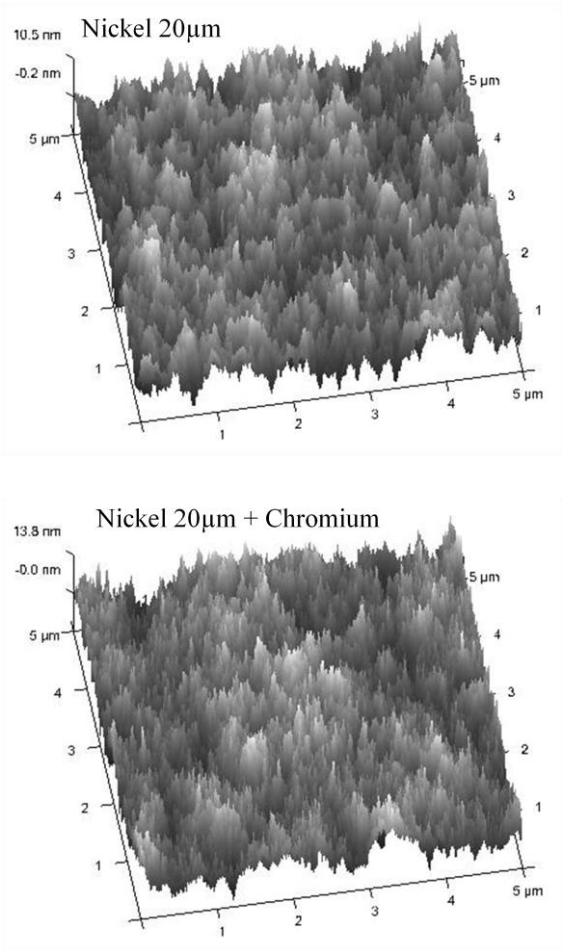


Figure 6.5 AFM 3D images of the nickel deposit with and without chromium as a topcoat

The thinner white Cu-Sn alloy plated to 0.5µm was visually very similar to the nickel deposit, Figure 6.6 shows the 3D image of the topography. The Rmax value of 73nm and RMS value of 8.3nm identified it as being a rougher deposit in comparison to the nickel. The chromium as a topcoat has an Rmax value of 33.7nm and RMS value of 5.61nm bringing the roughness closer to the standard nickel and chromium deposit.

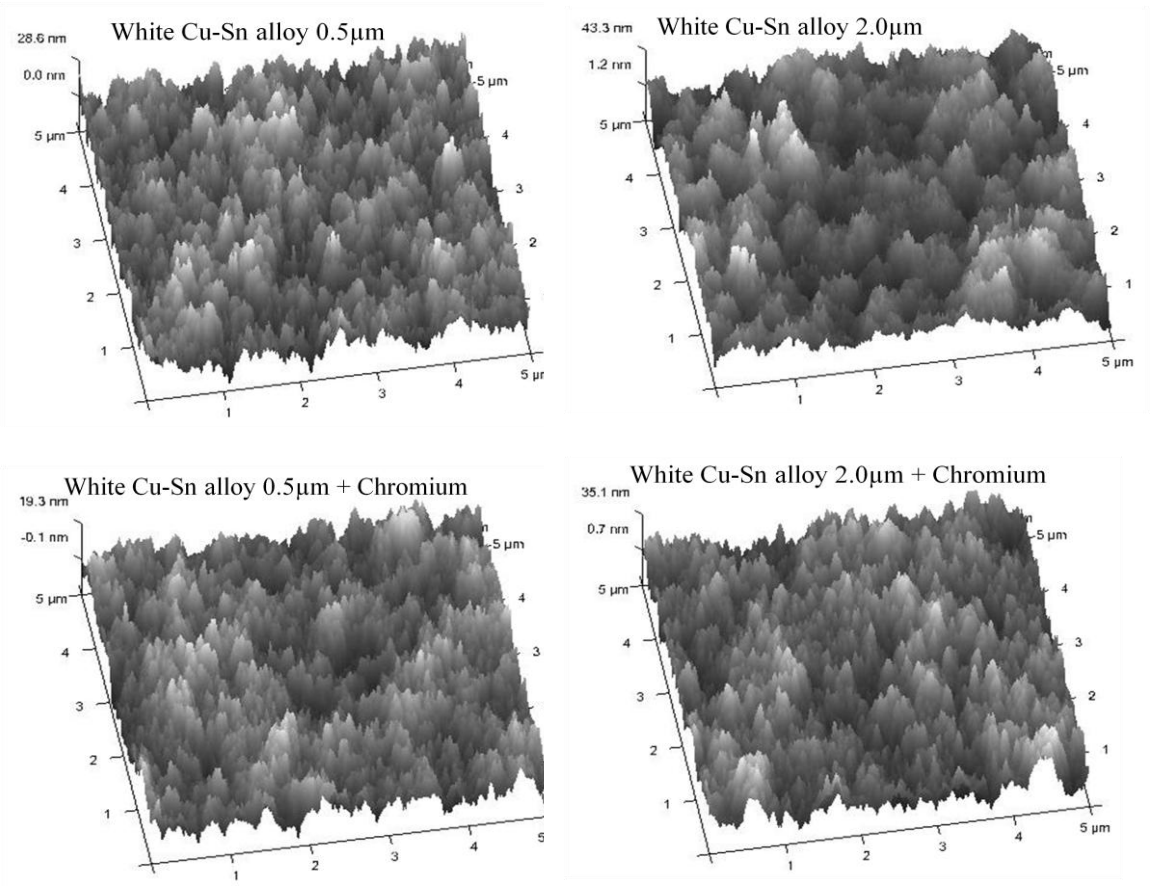


Figure 6.6 AFM 3D images of the white Cu-Sn alloy deposit with and without the chromium deposit as a topcoat.

Increasing the thickness of the white Cu-Sn alloy deposit to 2.0µm increases the roughness compared to the 0.5µm white Cu-Sn alloy, the Rmax value is 166nm and the RMS value is 12nm, thus in comparison to the nickel deposit is much rougher. Chromium as the topcoat gives a Rmax value of 80nm and RMS value of 9.84nm, still maintaining increased roughness of the deposit compared to the standard nickel and chromium deposit. Visually, the 2.0µm white Cu-Sn alloy shows a background haze that would not be identified by the spectrophotometer, but the AFM results identify a rougher deposit with more light scatter, thus coinciding with the haze visually seen in the deposit.

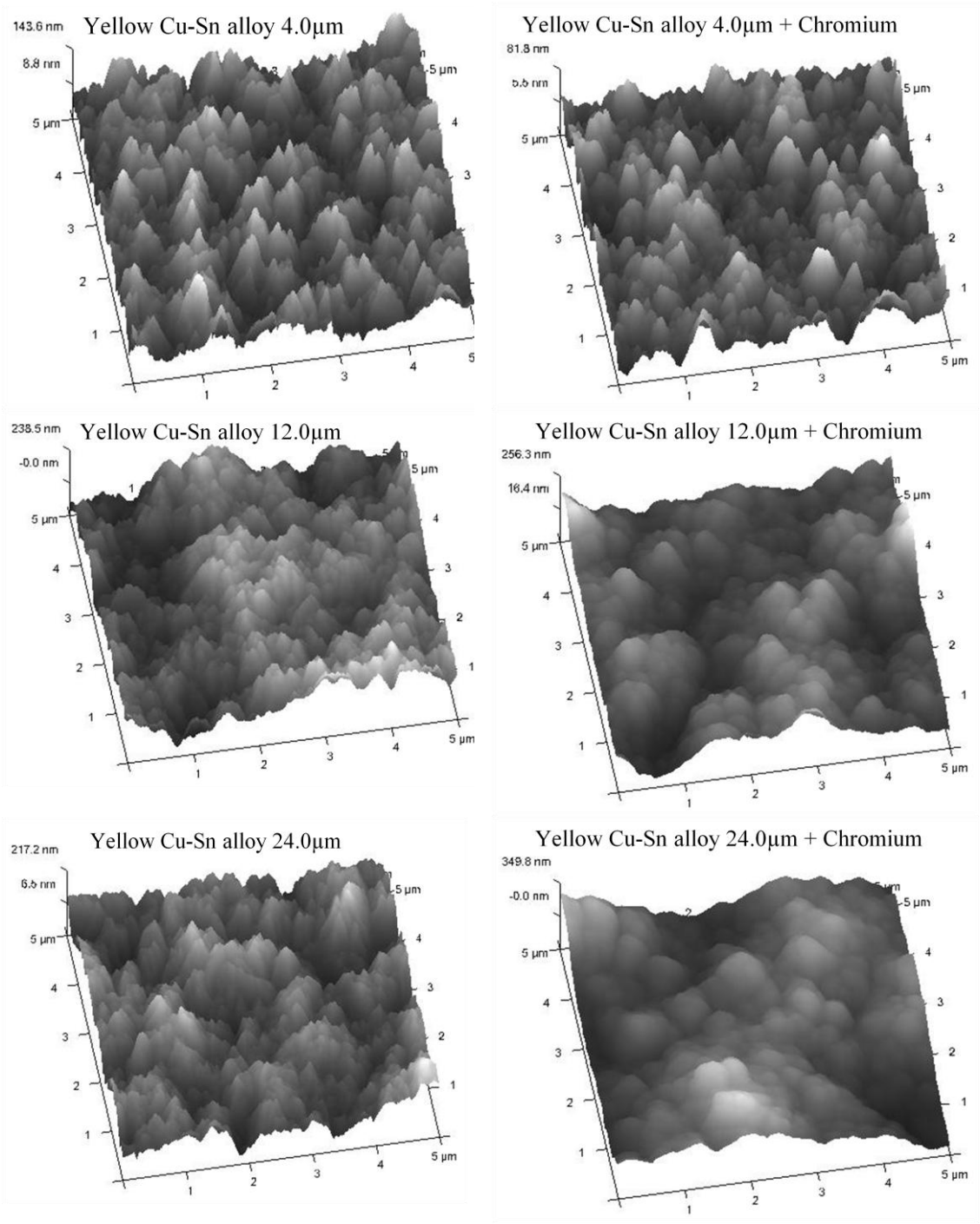


Figure 6.7 AFM 3D images of the yellow Cu-Sn alloy deposit with and without the chromium deposit as a topcoat.

The AFM image of the yellow Cu-Sn alloy plated to a thickness of 4.0µm is shown in Figure 6.7, visually the deposit is dull and has increased roughness. The Rmax value is 276nm and the RMS value is 41.2nm, which is considerably rougher

compared to the nickel deposit. It appears chromium as a topcoat reduces the roughness of the deposit giving a Rmax value of 150nm and RMS value of 22.9nm, which is rougher than the standard nickel and chromium deposit.

The 12µm yellow Cu-Sn alloy has increased roughness compared to the thinner 4.0µm yellow Cu-Sn alloy, the images can be seen in Figure 6.7. The roughness results of the 12µm yellow Cu-Sn alloy gave a Rmax value of 452nm and RMS value of 71.4nm, visually the deposit looks very matt and uneven, suggesting the light is being scattered in all directions due to the roughness of the deposit. The chromium as a topcoat has an Rmax value of 464nm and a RMS value of 66.4nm, this is significantly rougher than the standard nickel and chromium deposit.

The AFM image can be seen in Figure 6.7 for the 24µm yellow Cu-Sn alloy, result shows a reduced roughness to the finish compared to the 12µm yellow Cu-Sn alloy with a Rmax value of 408nm and RMS value of 60.8nm, thus is still much rougher than the standard nickel deposit but it is unclear why the 12µm yellow Cu-Sn alloy is rougher than the 24µm yellow Cu-Sn alloy deposit. The chromium as a topcoat on the 24µm yellow Cu-Sn alloy has the roughest deposit giving a Rmax value of 639nm and RMS value of 107nm. The nodulations visible in the SEM image, Figure 6.3, could be attributed to this increased roughness with a matt and uneven visual appearance. Overall the 4µm, 12µm and 24µm yellow Cu-Sn alloy deposits with chromium are not similar to the nickel with chromium deposit, therefore visually would not be suitable alternative to it.

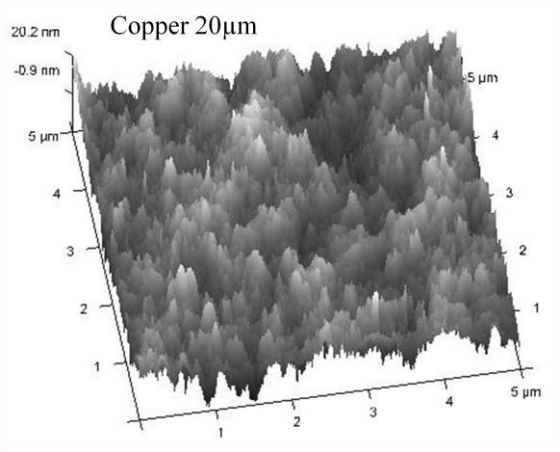


Figure 6.8 AFM 3D images of the copper deposit.

The copper deposit was also analysed to confirm if it would influence the roughness of the white or yellow Cu-Sn alloy deposits plated on top. The copper deposit gave a Rmax value of 58nm and RMS value of 5.92nm, Figure 6.8 shows the AFM image of the copper deposit. Visually the deposit was bright and reflective but AFM results show it is rougher than the standard nickel panel. The Cu-Sn alloy deposits have higher RMS values compared to the copper and therefore indicate that the copper did not influence the roughness of the white or yellow Cu-Sn alloy deposit.

6.3 Electrochemical corrosion resistance results

6.3.1 Linear polarisation results

Linear polarisation was used to obtain the corrosion current values, which were used to calculate the estimated corrosion rate of each electroplated deposit using equation 6.1. A study by Kouril et al uses the linear polarisation technique to calculate the polarisation resistance (Rp) of corroding reinforcements used in concrete (Kouril 2006).

$$MPY = I\text{corr}\,(\Lambda)(1/\rho)(\varepsilon) \qquad (6.1)$$

Where

MPY	= mils per year (1mil is equal to 0.0245mm if conversion is required)
I_{corr}	= the corrosion current density in amps/cm^2
Λ	= a combination of several conversion terms and is 1.2866x10^5 [equivalents .sec.ml]/[Coulombs.cm.year]
ρ	= the metal density in grams/cm^3
ε	= the equivalent weight of the metal in grams (equivalent weight is the molecular weight of the metal divided by the number of electrons in the anodic half reaction)

The figures used for the calculation of the corrosion rate according to Weast are as follows: (Weast 1980)

	Density	Electrons in the anodic half equation
Nickel	= 8.9g/cm^2	2
Chromium	= 7.18g/cm^2	3
Yellow and white Cu-Sn alloy	= 8.5g/cm^2	2

Table 6.3 shows the results of the polarisation resistance, corrosion current and the calculated estimated corrosion rate of each electroplated deposit. The polarisation resistance gives an indication of resistance to corrosion in Kohms cm^{-1}. Average corrosion current quantifies the current associated with corrosion of the deposit expressed in nA/cm^2. Corrosion rate expressed in mm/year describes the rate of corrosion of the deposit.

Panel Identification	**Polarisation resistance (R_p) KΩ cm^{-1}**	**Average I_{corr} (nA/cm^2)**	**Corrosion rate (mm per year)**
Nickel 20µm	47	482	7.13
Nickel 20µm + Chromium	328	77	0.60
White Cu-Sn alloy 0.5µm	156	197	9.15
White Cu-Sn alloy 2.0µm	337	98	4.43
White Cu-Sn alloy 0.5µm + chromium	207	108	0.85
White Cu-Sn alloy 2.0µm + chromium	171	132	1.02
Yellow Cu-Sn alloy 4.0µm + White Cu-Sn alloy 0.5µm	17	1848	174
Yellow Cu-Sn alloy 12.0µm + White Cu-Sn alloy 0.5µm	63	672	63.5
Yellow Cu-Sn alloy 24.0µm + White Cu-Sn alloy 0.5µm	104	273	25.8
Yellow Cu-Sn alloy 4.0µm + White Cu-Sn alloy 0.5µm + chromium	22	1232	9.55
Yellow Cu-Sn alloy 12.0µm + White Cu-Sn alloy 0.5µm + chromium	41	903	7.00
Yellow Cu-Sn alloy 24.0µm + White Cu-Sn alloy 0.5µm + chromium	14	1490	11.5

Table 6.3 Linear polarisation techniques used to obtain the polarisation resistance, corrosion current and calculated estimated corrosion rate results for all electroplated deposits.

Figures 6.9, 6.10 and 6.11 show the linear polarisation graphs for the electroplated nickel deposit with and without chromium, the white Cu-Sn alloy with and without chromium and the yellow Cu-Sn alloy with and without chromium respectively.

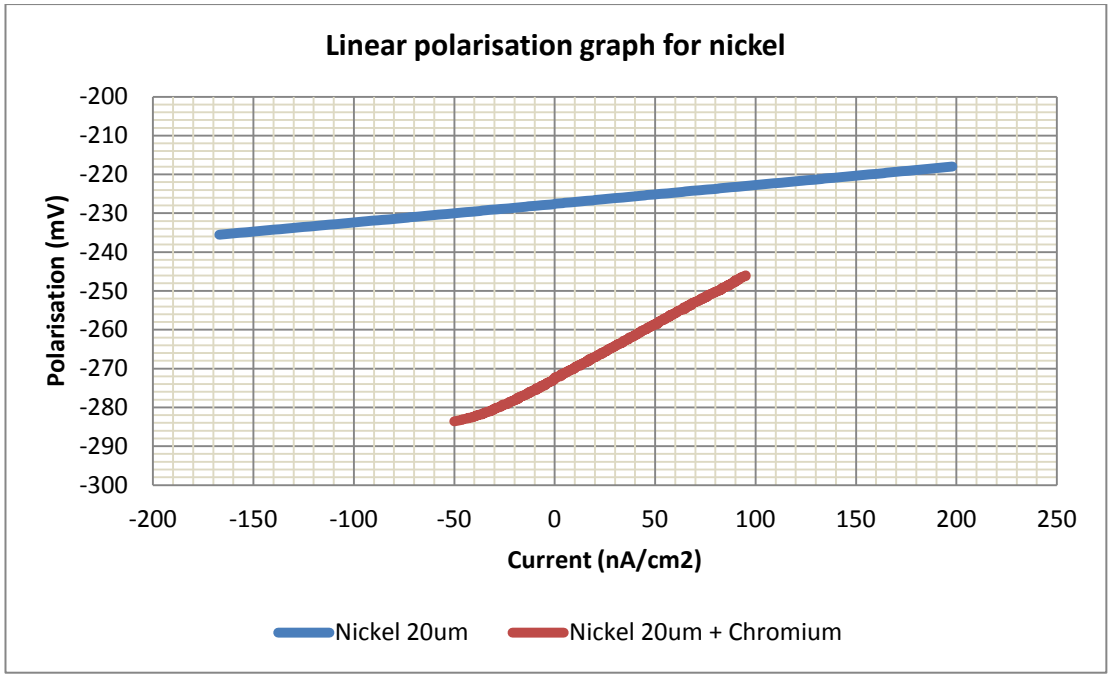


Figure 6.9 Linear polarisation graph for the nickel deposit with and without chromium as a topcoat

The nickel deposit has a corrosion rate of 7.13mm per year and with chromium plated as a topcoat the corrosion rate is calculated as 0.60mm per year. This shows that the chromium deposit can significantly reduce the corrosion rate and provide corrosion protection to the nickel deposit.

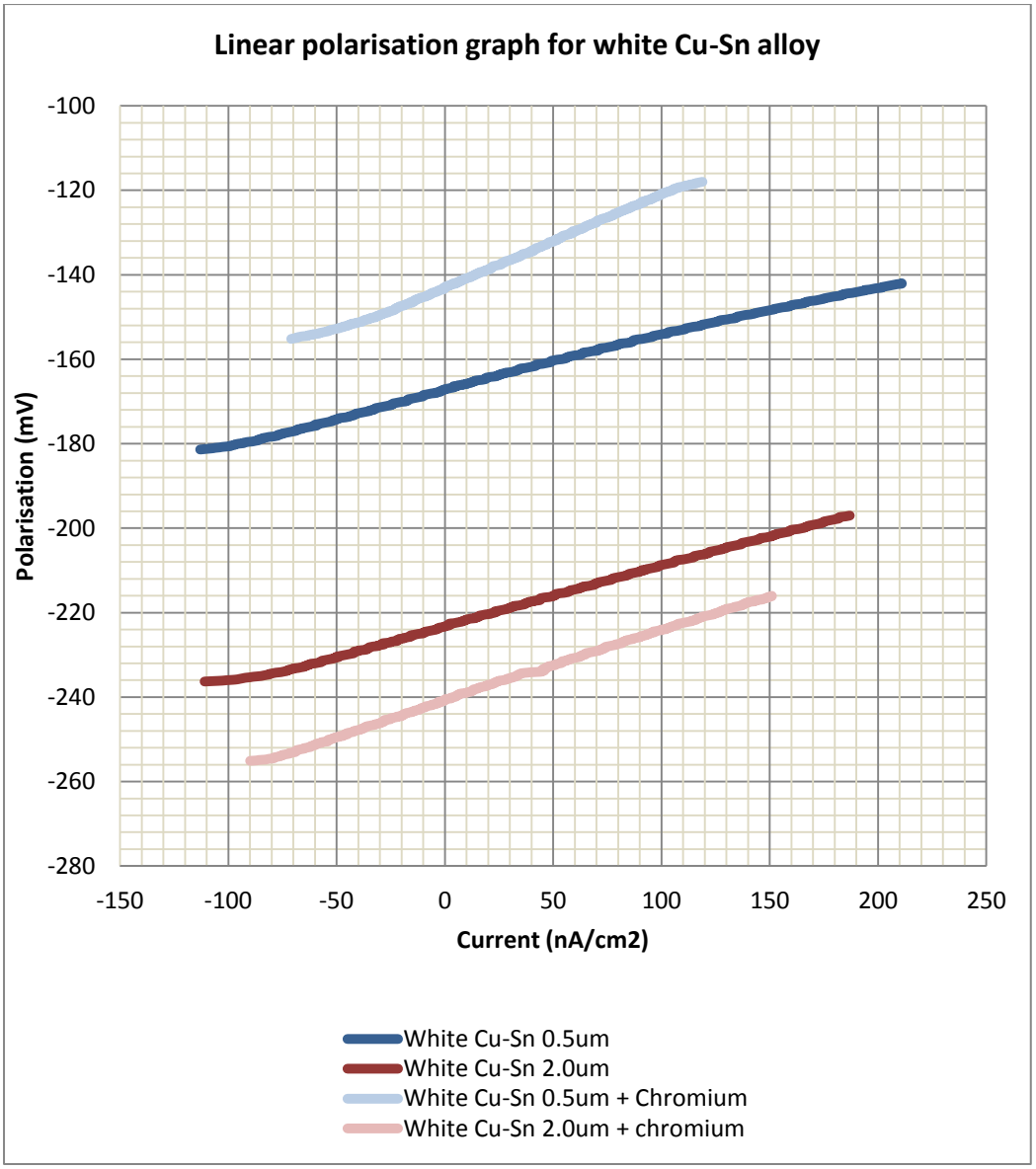


Figure 6.10 Linear polarisation graph for the white Cu-Sn alloy deposit with and without chromium as a topcoat.

The white Cu-Sn alloy plated to a thickness of 0.5µm has a corrosion rate of 9.15mm per year but with the chromium deposit as a topcoat the corrosion rate is calculated at 0.85mm per year. This suggests that the nickel deposit is more corrosion resistant than the 0.5µm white Cu-Sn alloy, although the linear polarisation result in Table 6.3 show the 0.5µm Cu-Sn alloy to have a higher polarisation resistance than the nickel. The linear polarisation result implies that the 0.5µm white Cu-Sn alloy has a lower corrosion current than the nickel and therefore it is more corrosion resistant. The

contradiction in these results could be due to the assumptions made with the calculation and therefore the linear polarisation results are thought to be more realistic and therefore deemed more reliable. On the other hand the linear polarisation results show the nickel with chromium deposit to be more corrosion resistant than the 0.5µm white Cu-Sn alloy with chromium. The calculation is based on equation 6.1.

The white Cu-Sn alloy plated to a thickness of 2µm has a calculated corrosion rate of 4.43mm per year, thus suggesting that it is more corrosion resistant than the 0.5µm white Cu-Sn alloy and nickel deposits with a corrosion rate of 9.15 and 7.13 respectively. This result is also supported by the higher polarisation resistance from the linear polarisation results. When chromium is plated onto the 2.0µm white Cu-Sn alloy the corrosion rate decreases from 4.43mm per year to 1.02mm per year. This is a faster corrosion rate than the 0.5µm white Cu-Sn alloy with chromium and nickel with chromium which have the corrosion rates of 0.85mm and 0.60mm per year respectively. The corrosion rate results show that increasing the thickness of the white Cu-Sn alloy does not improve the corrosion resistance.

This set of linear polarisation results show that the white Cu-Sn alloy could have the potential to be more corrosion resistant than nickel if the deposit could be plated thicker, since the polarisation resistance increases with thickness of the white Cu-Sn alloy. The next stage of study therefore aimed to improve upon the thickness of the Cu-Sn alloy deposit in order to improve the corrosion protection of the substrate. This was achieved by plating a yellow Cu-Sn alloy which is commercially plated thicker than white Cu-Sn alloy. Using the 0.5µm white Cu-Sn alloy deposit as a top

coat to the yellow Cu-Sn alloy to give it the silver coloured appearance means there is an overall thicker deposit which eliminates the appearance defect associated with a thicker white Cu-Sn alloy deposit.

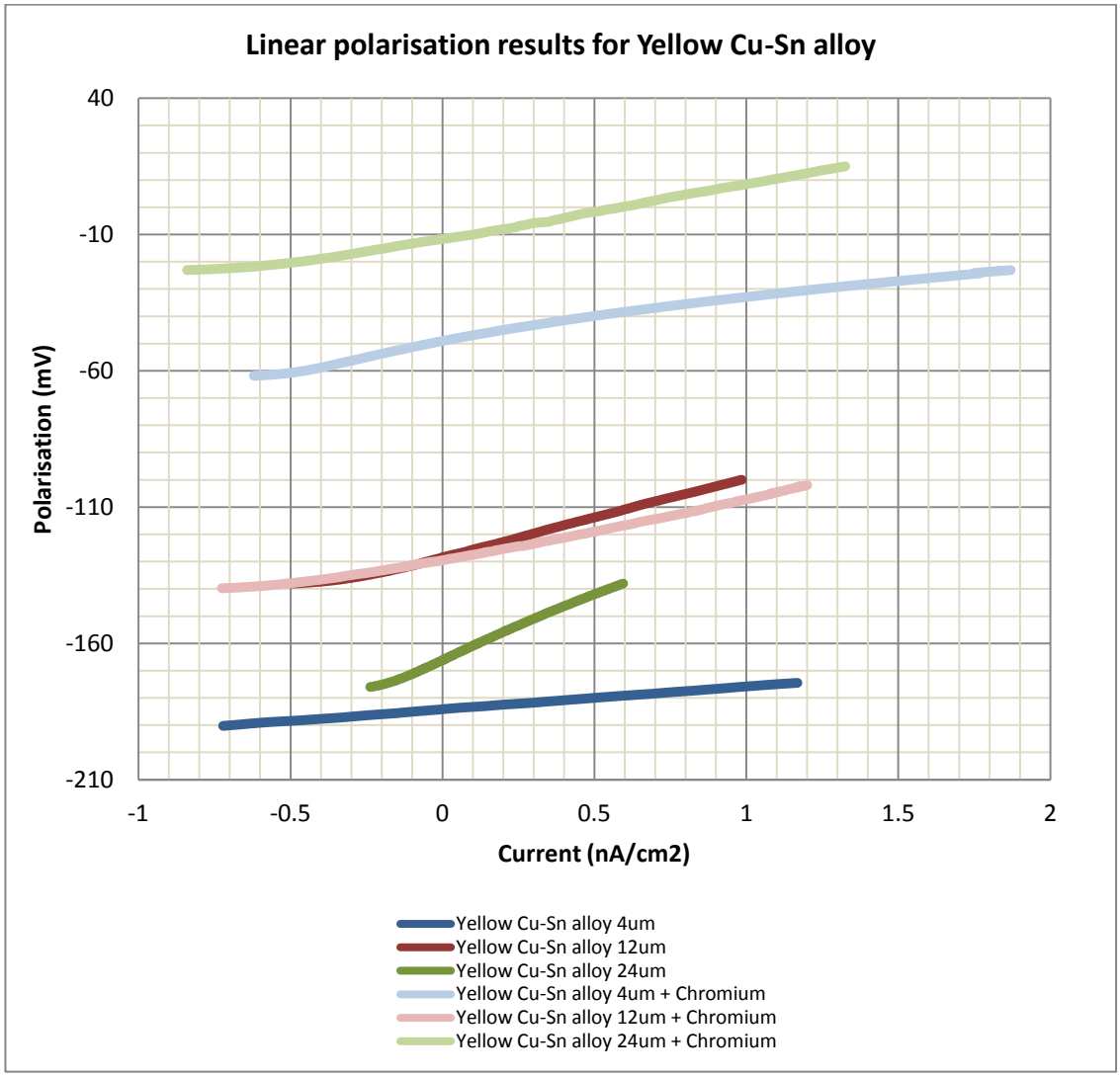


Figure 6.11 Linear polarisation graph for the yellow Cu-Sn alloy deposit with and without chromium as a topcoat.

The yellow Cu-Sn alloy was plated to a thickness of 4µm, 12µm and 24µm each with 0.5µm of white Cu-Sn alloy plated on top, these deposits showed a much higher calculated corrosion rate of 174, 63.5, 25.8 mm per year respectively. The polarisation resistance values in Table 6.3 calculated from the slope of the linear polarisation graph (Figure 6.11) support the calculated corrosion rates of the yellow Cu-Sn alloy deposit which confirms an increase in corrosion resistance the thicker the deposit is plated. The polarisation resistance values obtained are slightly higher than for the nickel deposit, suggesting that the yellow Cu-Sn alloy deposits now have an improved corrosion resistance with increased deposit thickness.

The yellow Cu-Sn alloy plated at varying thicknesses with 0.5µm white Cu-Sn alloy and chromium deposit plated on top, have higher corrosion resistance compared to the deposits without chromium deposit (Table 6.3). The conclusion is that chromium provides additional corrosion protection. The 4µm, 12µm and 24µm yellow Cu-Sn alloy deposits with 0.5µm white Cu-Sn alloy and chromium plated on top have corrosion rates of 9.55, 7.0, and 11.5 mm per year respectively. These figures are still higher than the case of nickel with chromium deposit which hast a corrosion rate of 0.6 mm per year, thus suggesting that this arrangement with white Cu-Sn alloy plated onto yellow Cu-Sn alloy will not be a suitable alternative to the nickel with chromium deposit.

6.3.2 Electrochemical impedance spectroscopy results

Electrochemical impedance spectroscopy (EIS) was used to interpret the electrochemical behaviour of the electroplated deposits and was represented as an equivalent circuit. Figures 6.12a, 6.12b and 6.12c show the Nyquist and Bode plots

and the equivalent circuit used to fit the data respectively. It shows the simulated data with the experimental data obtained in this study (Tait 1994). The equivalent circuit is made up of resisters and constant phase element, instead of pure capacitors. This gives a more accurate fitting of the simulated data with the experimental data. Two time constants are observed, one at high frequency, expected to be the electroplated deposit/electrolyte interface and the other at low frequencies expected to be the passive oxide layer (Arslan 2008).

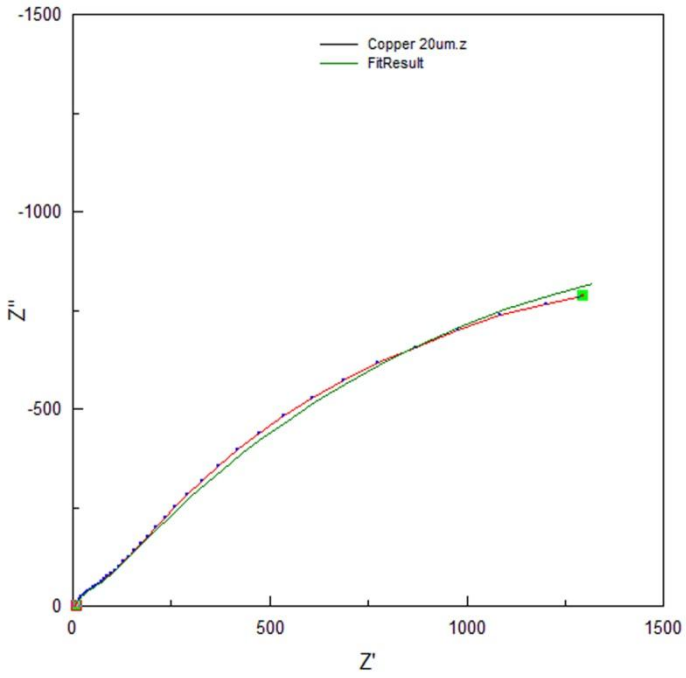


Figure 6.12a Example shown is of the copper deposit with fit results overlaid in the Nyquist plot.

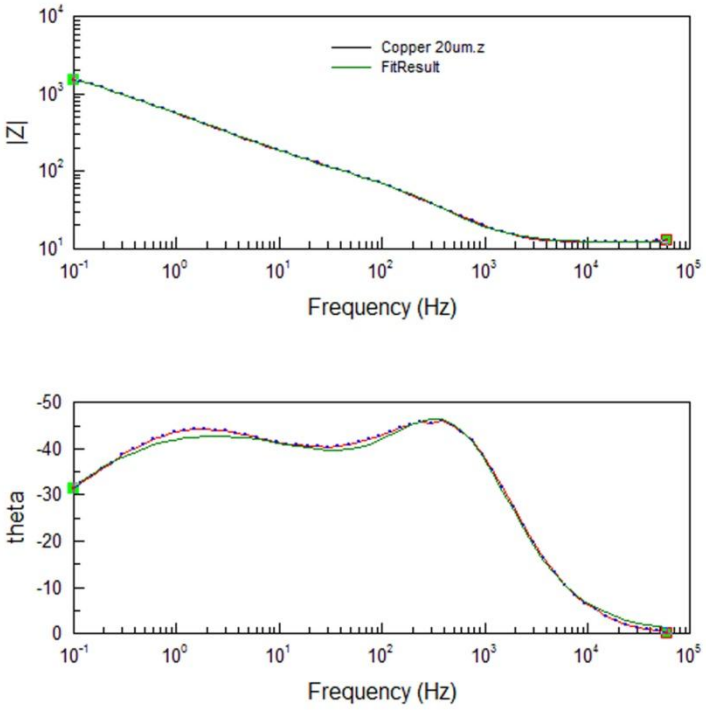


Figure 6.12b Example shown is of the copper deposit with fit results overlaid in the Bode plot.

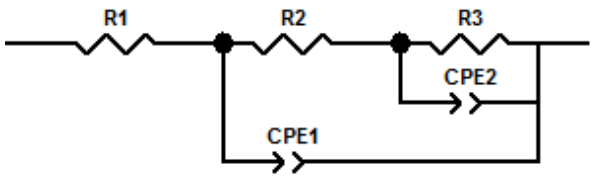


Figure 6.12c Equivalent circuit used to fit the EIS data for all electroplated deposits.

Figure 6.12c shows the equivalent circuit where R1 represents the solution resistance, R2 is the resistance of the electroplated deposit and R3 is the resistance of the passive oxide layer. CPE1 represents the constant phase element of the electroplated deposit and CPE2 is the constant phase element of the passive oxide layer. For this study R2 and R3 have been added together to give an overall polarisation resistance of the deposit to enable comparison with other deposits.

Table 6.4 shows the EIS experimental data to fit the equivalent circuit and Figures 6.13a and 6.13b show the Nyquist and Bode plots respectively for the nickel with and without chromium deposits, Figures 6.14a and 6.14b show the Nyquist and Bode plots respectively for the white Cu-Sn alloy with and without chromium and Figures 6.15a and 6.15b show the Nyquist and Bode plots respectively for the yellow Cu-Sn alloy with and without chromium. Figure 6.12a and 6.12b show the Nyquist and Bode plot respectively of the copper and an example of the simulated fit data using the equivalent circuit shown in Figure 6.12c.

Panel identification	**Polarisation resistance R_p ($K\Omega\ cm^{-1}$)**	**CPE_1 $x10^{-5}$ (Farad)**	**CPE_2 $x10^{-4}$ (Farad)**
Nickel 20µm	36.1	1.2752	0.6421
Nickel 20µm + Chromium	22.1	7.0763	1.7562
White Cu-Sn alloy 0.5µm	17.3	2.6074	1.5468
White Cu-Sn alloy 2.0µm	17.3	3.6444	3.9618
White Cu-Sn alloy 0.5µm + chromium	8.7	4.5903	6.8690
White Cu-Sn alloy 2.0µm + chromium	13.5	4.9812	6.7480
Yellow Cu-Sn alloy 4.0µm	0.178	6.7232	2.0780
Yellow Cu-Sn alloy 12.0µm	2.6	17.670	16.185
Yellow Cu-Sn alloy 24.0µm	3.3	1.3094	1.8789
Yellow Cu-Sn alloy 4.0µm + chromium	8.8	4.1168	9.8390
Yellow Cu-Sn alloy 12.0µm + chromium	14.1	1.4041	0.4123
Yellow Cu-Sn alloy 24.0µm + chromium	14.0	1.2311	8.4956

Table 6.4 EIS results for all electroplated deposits

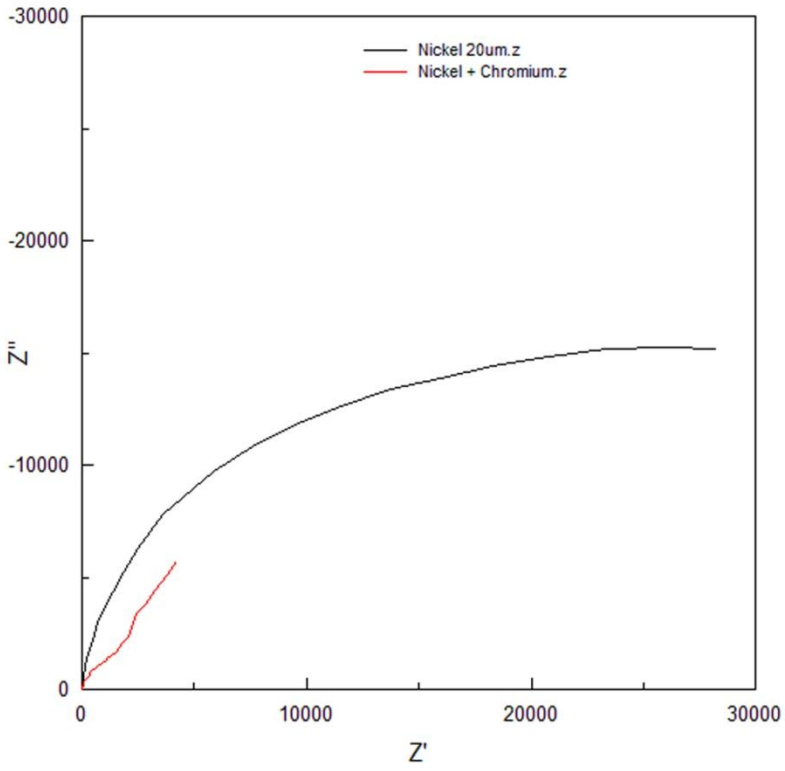


Figure 6.13a Nyquist plot for the nickel deposit with and without chromium

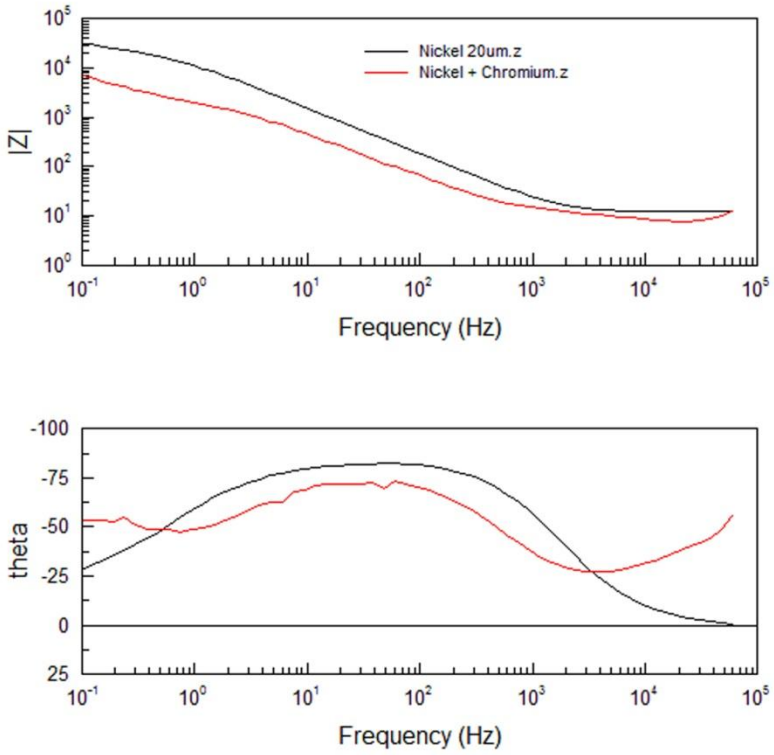


Figure 6.13b Bode plot for the nickel deposit with and without chromium

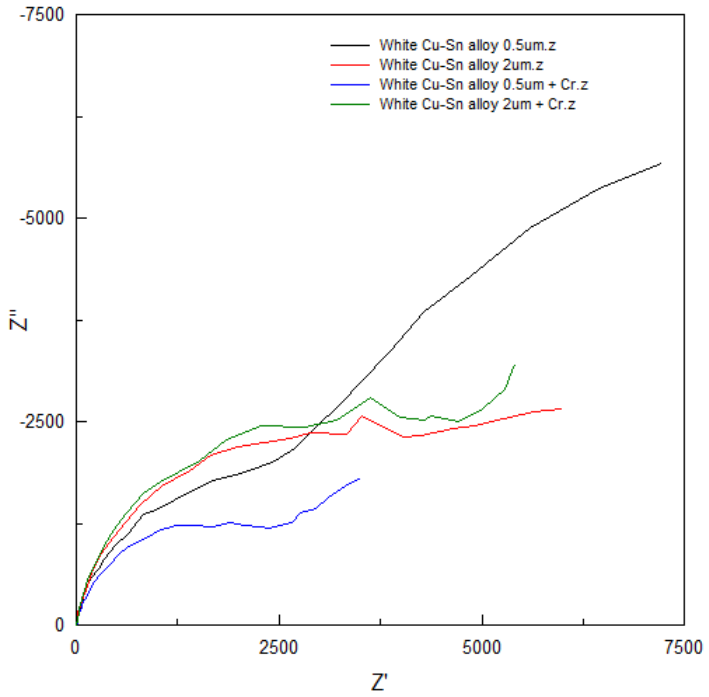


Figure 6.14a Nyquist plot for the white Cu-Sn alloy deposit with and without chromium

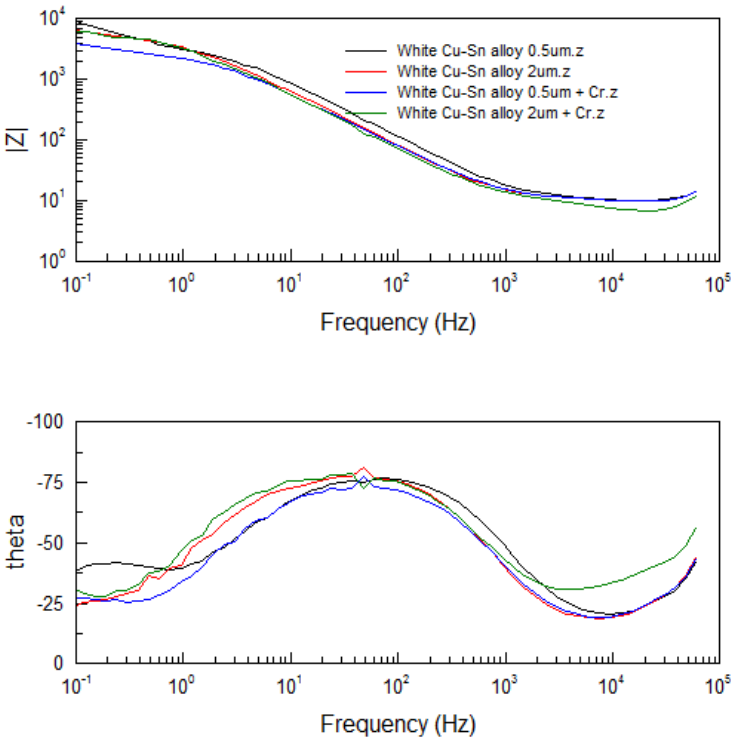


Figure 6.14b Bode plot for the white Cu-Sn alloy deposit with and without chromium

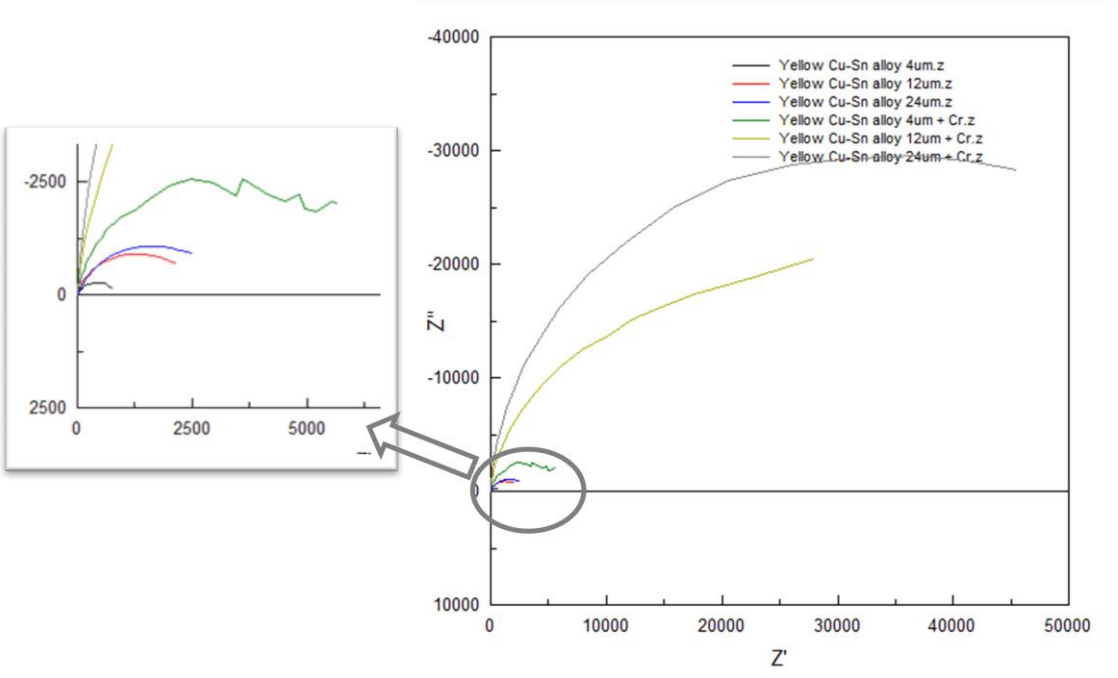


Figure 6.15a Nyquist plot for the yellow Cu-Sn alloy deposit with and without chromium

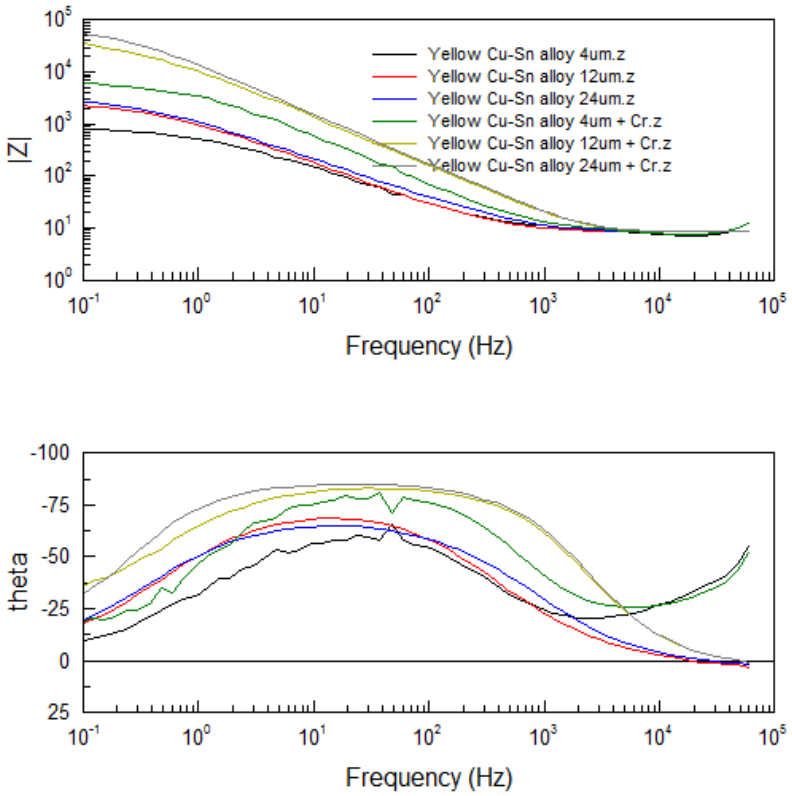


Figure 6.15b Bode plot for the yellow Cu-Sn alloy deposit with and without chromium

The impedance spectra is displayed in two forms, the first being the Nyquist plot, depicting a plot of the imaginary part of the impedance against the real part of the impedance and the second being the Bode plot, showing the modules of the impedance and the phase angle as a function of the frequency.

A study by Girault et al (Girault 2001) gives an equivalent circuit for the interpretation of a passivated nickel deposit, although this is not directly related to this study but it does confirm that chromium oxidises to give a protective chromium oxide layer and with a similar impedance spectra it is feasible to use the same equivalent circuit. The equivalent circuit is also supported by Arslan et al (Arslan 2008) and shows an oxide layer on a titanium substrate, the equivalent circuit is shown in Figure 6.12c.

The constant phase element CPE1 represents the surface of the metallic deposit with the polarisation resistance as R2, the constant phase element CPE2 represents the surface of the oxide layer with the polarisation resistance as R3. The addition of R2 with R3 would give the overall polarisation resistance, Rp of the deposit.

The oxide layer will be identified in the high frequency areas while the low frequency areas show the response of the metallic layer with the metal/solution interface at the bottom of the pores (Girault 2001). The equivalent circuit did not always clearly fit the high frequency data, this could be due to a third time constant that was not identified and therefore could not be confirmed in this study. With the results obtained, the selected equivalent circuit in Figure 6.12c was still the best fit to the data collected. The EIS work carried out did identify two time constants as the

Bode plot showed a flattened semicircle while the Nyquist plot did not fit the simulated one time constant equivalent circuit.

The two time constants could be explained as the two different electroplated deposits, for example the nickel and chromium deposit, the chromium is only plated to a thickness of 0.3µm and therefore it is most likely to be porous, thus exposing small areas of nickel. If this is the case the equivalent circuit in Figure 6.12c would show the CPE1 to be chromium and CPE2 to be nickel with any oxide layer missing from the data.

The constant phase element with a value in the region of $5x10^{-5}$ Farad indicates metallic corrosion, which is the case for most of CPE1 values achieved in this study with the exception of the 12µm yellow Cu-Sn alloy deposit having a value of 10^{-6} (Arslan 2008). The CPE1 results in Table 6.4 suggest that part of the equivalent circuit is a metallic deposit corroding in the salt solution. The topography of the yellow Cu-Sn alloys shows that the surface is rougher than the other deposits. An increase in surface roughness is an indication that the overall surface area is larger than the required area of $1cm^2$, as a consequence, the CPE value could be higher than expected.

The CPE2 value is in the region of 10^{-4}, this indicating neither metallic corrosion nor the presence of an oxide layer. Using the equivalent circuit in Figure 6.12c, CPE2 was suggested as an oxide layer but this has been ruled out due to the high values obtained. It is possible that the metallic layer underneath the top layer is also contributing as a result of the top layer being porous, although this layer would have

a small area exposed through the pores, therefore the expected CPE2 value should be much smaller than the CPE1 value. The results obtained do not support this theory and therefore suggest that the full interpretation of the EIS data is not understood, additional investigation therefore will be recommended for further work.

6.4 Accelerated corrosion testing results

The evaluation of the deposits was carried out by visual examination and guided by the specification ASTM B 537-70 (ASTM 2007). It is determined by the percentage of corrosion that covers both the deposit and substrate. The corrosion rating is given two values x/y, where 'x' refers to the coverage and appearance of the substrate corrosion (known as the protection rating) and 'y' refers to the coverage and appearance of the coating itself and is known as the appearance rating. All ratings are given a value of 1-10 with 10 being the best (no corrosion) and 1 being the worst (corrosion seen all over the specimen).

Accelerated corrosion tests were used to assess the corrosion resistance of deposits under the specified conditions, to compare with other deposits exposed to the same conditions. Two accelerated corrosion tests were carried out in this study, one being the neutral salt spray test (NSS) and the second being the copper accelerated acetic acid salt spray (CASS). CASS is the more aggressive test out of the two and therefore NSS is often used for less corrosion resistant deposits. A study by Figueiredo et al used the NSS accelerated corrosion test ASTM B 117 specification (as used in this study) to corrode a bronze-lead alloy, the deposit was evaluated after 120 and 1000 hours and the corrosion products were analysed using the SEM. In a

separate study Schutz et al used CASS to characterise the degradation of painted mirrors, they also used the NSS test which generated the same results, but the CASS test produced results in a faster time since it was a more aggressive test (Schutz 1997).

Both the NSS and CASS tests were used to assess all the deposits under evaluation in this study. The standard duplex nickel and chromium deposit were evaluated using the CASS accelerated test within the electroplating industry because of their higher corrosion resistance. This study only looked at the bright nickel and chromium deposits, which were less corrosion resistant compared to the duplex nickel and chromium deposits. The nickel and chromium deposits survived many hours in the NSS test before corrosion commenced and therefore the test was time consuming. On the other hand CASS accelerated test would have been more appropriate but was be too aggressive for the nickel panel with no chromium deposit. Therefore a combination of NSS and CASS accelerated tests were sufficient to accurately test all deposits under evaluation.

6.4.1 Neutral salt spray corrosion test results

Neutral salt spray (NSS) corrosion testing was carried out continuously over a 72 hour period with observation and corrosion rating given every 24 hours. The test was stopped after 72 hours due the deterioration of some of the Cu-Sn alloy and nickel deposit without the chromium as a topcoat. The results are presented in Table 6.5.

Panel identification	**NSS 24 hours**	**NSS 48 hours**	**NSS 72 hours**
Nickel 20µm	10/2	8/2	3/1
Nickel 20µm + Chromium	10/10	10/10	10/10
White Cu-Sn alloy 0.5µm	5/5	4/3	2/1
White Cu-Sn alloy 2.0µm	4/4	4/4	3/2
White Cu-Sn alloy 0.5µm + chromium	8/8	5/5	4/2
White Cu-Sn alloy 2.0µm + chromium	8/8	6/5	4/2
Yellow Cu-Sn alloy 4.0µm + White Cu-Sn alloy 0.5µm	3/1	2/1	1/1
Yellow Cu-Sn alloy 12.0µm + White Cu-Sn alloy 0.5µm	3/1	2/1	1/1
Yellow Cu-Sn alloy 24.0µm + White Cu-Sn alloy 0.5µm	3/2	2/1	2/1
Yellow Cu-Sn alloy 4.0µm + White Cu-Sn alloy 0.5µm + chromium	5/3	4/2	2/2
Yellow Cu-Sn alloy 12.0µm + White Cu-Sn alloy 0.5µm + chromium	6/3	4/3	2/2
Yellow Cu-Sn alloy 24.0µm + White Cu-Sn alloy 0.5µm + chromium	6/3	5/3	3/2

Table 6.5 NSS results for all electroplated deposits

The evaluation of the nickel panel showed that within the first 24 hours it had a corrosion rating of 10/2, highlighting very little corrosion resistance but still offered protection to the substrate. As the test continued the nickel panel showed signs of corrosion to the substrate, and after 48 hours it no longer protected the substrate which continued to corrode until the test was stopped at 72 hours. The nickel with chromium deposit also displayed a higher corrosion resistance in the NSS since no visible corrosion was identified, and a corrosion rating of 10/10 after 72 hours was achieved when the test was finally stopped. The NSS accelerated test therefore clearly shows that chromium is essential to achieving the best corrosion performance since the nickel deposit alone only lasts 24 hours before substrate corrosion is seen.

The white Cu-Sn alloy plated at 0.5µm showed significant corrosion to both the substrate and deposit in the first 24 hours of NSS with a corrosion rating of 5/5, thus

showing a higher corrosion resistance than the nickel deposit but providing less corrosion protection to the substrate. As the test continued, increased corrosion was seen on the 0.5µm white Cu-Sn alloy deposit and the substrate which reduced the corrosion ratings to 4/3 and 2/1 at 48 and 72 hours respectively. Overall the 0.5µm white Cu-Sn alloy deposit is more corrosion resistant than the nickel deposit but it does not provide the same corrosion protection to the substrate, overall it would not be a suitable replacement for applications requiring corrosion protection.

The chromium plated onto the 0.5µm white Cu-Sn alloy had improved corrosion resistance with a corrosion rating of 8/8 after 24 hours, the corrosion rating reduced to 4/2 by the end of the test as more corrosion became visible. This shows that the 0.5µm white Cu-Sn alloy with chromium is less corrosion resistant than the nickel with chromium deposit and therefore not a suitable alternative.

The thicker white Cu-Sn alloy plated to 2.0µm provided a corrosion rating of 4/4 after 24 hours, by the end of the test the 2.0µm white Cu-Sn alloy had a corrosion rating of 3/2. The corrosion resistance of the deposit shows a slight improvement compared to the nickel and 0.5µm Cu-Sn alloy deposits and therefore provided a potential alternative to the nickel deposit. The 2.0µm white Cu-Sn alloy did have a small improvement on the corrosion resistance compared to the thinner 0.5µm white Cu-Sn alloy deposit, thus showing that a thicker white Cu-Sn alloy deposit improves the corrosion resistance.

The chromium plated onto the 2.0µm white Cu-Sn alloy helped improve the corrosion protection of the substrate giving a corrosion rating of 8/8 after 24 hours,

by 72 hours the corrosion rating was recorded as 4/2. The 2.0µm white Cu-Sn alloy with chromium did not have the same corrosion resistance as the nickel with chromium deposit, thus suggesting it would corrode faster and therefore would not be a suitable alternative.

The yellow Cu-Sn alloy plated to three different thicknesses 4.0µm, 12.0µm and 24µm was tested to confirm if there could be a correlation between plating thickness and improved corrosion protection. The white Cu-Sn alloy was then plated on top of the yellow Cu-Sn alloy at a thickness of 0.5µm to provide the correct appearance.

The yellow Cu-Sn alloy plated to a thickness of 4.0µm with white Cu-Sn alloy on top showed poor corrosion resistance and protection of the substrate. After 24 hours the corrosion rating was 3/1 and by 72 hours it had a corrosion rating of 1/1. This offered very little corrosion protection to the substrate and there was no advantage over the white Cu-Sn alloy deposit. Plating chromium onto the 4µm yellow Cu-Sn alloy with 0.5µm white Cu-Sn alloy offered more protection to the substrate. The corrosion rating after 24 hours was 5/3, and by the end of the test it had a corrosion rating of 2/2. There was no improvement on the corrosion resistance of the white Cu-Sn alloy and chromium and therefore no advantage was gained. As an alternative to nickel with chromium deposit, the Cu-Sn alloy was concluded not to be a suitable alternative.

The yellow Cu-Sn alloy plated to a thickness of 12µm with 0.5µm white Cu-Sn alloy on top showed the same corrosion resistance as the thinner 4.0µm equivalent and therefore there was no advantage gained by thicker plating. The chromium plated

onto the duplex Cu-Sn alloy did improve the corrosion protection to the substrate with a corrosion rating after 24 hours of 6/3, which continued to corrode and after 72 hour it had a corrosion rating of 2/2. This shows that increasing the thickness of the yellow Cu-Sn alloy followed by the 0.5µm white Cu-Sn alloy and chromium did not improve the corrosion resistance significantly enough to be a suitable alternative to the nickel with chromium deposit.

The yellow Cu-Sn alloy plated to a thickness of 24µm followed by the 0.5µm white Cu-Sn alloy plated on top had similar corrosion ratings to the yellow Cu-Sn alloy plated to a thickness of 4.0µm and 12µm. After 24 hours the corrosion rating was 3/2 and by 72 hours it had corroded further and had a rating of 2/1. Increasing the thickness of the yellow Cu-Sn alloy did not entirely improve the corrosion resistance. The conclusion therefore is that a porous deposit is not the only factor that affects corrosion protection. The difference in alloy composition between the yellow and white Cu-Sn alloy may possibly change the corrosion resistance of a deposit. The yellow Cu-Sn alloy has a higher percentage of copper in the deposit compared to the white Cu-Sn alloy deposit which contains more tin. The NSS accelerated corrosion test has shown the two alloys to behave differently thus confirming that alloy composition is a factor in the corrosion resistant properties of the deposit. Overall the chromium plated on top of all duplex Cu-Sn alloys again improved corrosion protection to the substrate but did not match the corrosion protection given by the nickel with chromium.

This set of results show that the duplex Cu-Sn alloy had no advantage over the white Cu-Sn alloy in offering more corrosion resistance. Increasing the thickness of the

yellow Cu-Sn alloy did not show any significant improvement on the corrosion resistance and therefore leaves alloy composition as a dominant factor in determining corrosion resistance. The chromium plated on top did improve the corrosion resistance as seen with all deposits yet this could not compare with the corrosion resistance of nickel and chromium deposit. The nickel and chromium deposit proved to have a corrosion resistance far more superior to the rest of all the sample deposits tested.

6.4.2 Copper accelerated acetic acid salt spray corrosion test results

Copper accelerated acetic acid salt spray (CASS) corrosion testing was carried out continuously over a period of 16 hours with observation and corrosion rating given every 8 hours since it is a more aggressive test. The test was stopped after 16 hours due to the deterioration of the nickel deposit without chromium as a top coat. All results are presented in Table 6.6.

Panel identification	**CASS 8 hours**	**CASS 16 hours**
Nickel 20µm	2/2	1/1
Nickel 20µm + Chromium	10/10	10/8
White Cu-Sn alloy 0.5µm	4/4	2/2
White Cu-Sn alloy 2.0µm	4/4	4/4
White Cu-Sn alloy 0.5µm + chromium	7/7	6/6
White Cu-Sn alloy 2.0µm + chromium	6/6	5/5
Yellow Cu-Sn alloy 4.0µm + White Cu-Sn alloy 0.5µm	5/5	2/2
Yellow Cu-Sn alloy 12.0µm + White Cu-Sn alloy 0.5µm	5/5	3/3
Yellow Cu-Sn alloy 24.0µm + White Cu-Sn alloy 0.5µm	3/3	3/3
Yellow Cu-Sn alloy 4.0µm + White Cu-Sn alloy 0.5µm + chromium	8/6	6/5
Yellow Cu-Sn alloy 12.0µm + White Cu-Sn alloy 0.5µm + chromium	8/6	5/5
Yellow Cu-Sn alloy 24.0µm + White Cu-Sn alloy 0.5µm + chromium	9/6	6/6

Table 6.6 CASS results for all electroplated deposits

The results show that the nickel was almost completely corroded after 8 hours and was given a corrosion rating of 2/2 and continued to corrode until a rating of 1/1 was reached after 16 hours. The nickel with chromium as a topcoat provided significantly more corrosion protection and no corrosion was identified after 8 hours. Consequently it was given a corrosion rating of 10/10. After 16 hours only the chromium had started to corrode but the substrate was still being protected, therefore giving a corrosion rating of 10/8.

The white Cu-Sn alloy plated to a thickness of 0.5µm showed a corrosion rating of 4/4 after 8 hours because corrosion to the substrate and the deposit was visible. After 16 hours the 0.5µm white Cu-Sn alloy continued to corrode and was given a corrosion rating of 2/2. Overall the 0.5µm white Cu-Sn alloy had a better corrosion rating than the nickel deposit implying that it was more corrosion resistant and also

provided slightly more corrosion protection to the substrate. The chromium plated as a topcoat to the 0.5µm white Cu-Sn alloy had a corrosion rating of 7/7 after 8 hours and by 16 hours it was given a corrosion rating of 6/6. Results obtained showed that the 0.5µm white Cu-Sn alloy and chromium was less corrosion resistant compared to the nickel and chromium deposit, suggesting that the underlying deposit influences the corrosion protection of the chromium deposit. The 0.5µm white Cu-Sn alloy process proved not to be a suitable alternative to the nickel deposit as its corrosion protection was not substantial enough.

The white Cu-Sn alloy plated to a thickness of 2µm was given a corrosion rating of 4/4 after 8 hours and did not corrode any further, thus maintaining a corrosion rating of 4/4 after 16 hours. The results show that the 2.0µm white Cu-Sn alloy deposit has a higher corrosion resistance compared to the 0.5µm white Cu-Sn alloy implying that a thicker deposit is likely to be less porous and therefore have increased corrosion protection. The 2µm white Cu-Sn alloy deposit compared to the nickel deposit proved to be more corrosion resistant and therefore could be a potential alternative. The chromium plated onto the 2.0µm white Cu-Sn alloy had a corrosion rating of 6/6 after 8 hours and then 5/5 after 16 hours, thus exhibiting a similar corrosion performance to the 0.5µm white Cu-Sn alloy. Overall, the 2µm white Cu-Sn alloy with chromium deposit had a lower corrosion resistance than that of the nickel with chromium deposit, thus suggesting that the deposit under the chromium influences the corrosion resistance of the chromium. The 2µm white Cu-Sn alloy therefore, would not be a suitable alternative replacement for the nickel.

The yellow Cu-Sn alloy deposit plated in varying thicknesses and then plated with 0.5µm white Cu-Sn alloy deposit as a top coat to maintain a silver coloured finish. The 4µm yellow Cu-Sn alloy had a corrosion rating of 5/5 after 8 hours and then 2/2 after 16 hours, it was therefore similar to the 12µm yellow Cu-Sn alloy which had a corrosion rating of 5/5 after 8 hours and by 16 hours it had a reduced corrosion rating of 3/3. Increasing the thickness of the yellow Cu-Sn alloy to 24µm gave it a worse corrosion rating of 3/3 after 8 hours with no further corrosion after 16 hours. The faster corrosion in the first 8 hours for the 24µm Cu-Sn alloy deposit is not easy to explain. There are numerous factors that can influence alloy plating and therefore it could be possible that the low corrosion rating was due to a defect in the deposit. Defects in the deposit could provide a site for corrosion to start more rapidly. Overall the corrosion ratings indicated that the yellow Cu-Sn alloy did not improve corrosion resistance with thickness but all deposits provided slightly better corrosion protection to the substrate than the nickel deposit alone by the end of the 16 hour test. The corrosion rating also indicated that the yellow Cu-Sn alloy deposit had no advantage over the white Cu-Sn alloys since the best corrosion protection was from the 2.0µm white Cu-Sn alloy deposit.

The entire yellow Cu-Sn alloy with a top coat of 0.5µm white Cu-Sn alloy and chromium deposit showed that although the coating was corroding it still provided a little more protection to the substrate than the other alternative deposits. The 4µm yellow Cu-Sn alloy with 0.5µm white Cu-Sn alloy and chromium had a corrosion rating of 8/6 after 8 hours and then 6/5 after 16 hours, the 12µm yellow Cu-Sn alloy with 0.5µm white Cu-Sn alloy and chromium deposit had a corrosion rating of 8/6 after 8 hours and then 5/5 after 16 hours, thus being similar to the thinner 4µm

yellow Cu-Sn alloy deposit. The 24µm yellow Cu-Sn alloy with 0.5µm white Cu-Sn alloy and chromium had a corrosion rating of 9/6 after 8 hours, thus providing the best corrosion protection to the substrate seen in this study. After 16 hours it was 6/6 and therefore showed a similar corrosion protection to the substrate as the other yellow Cu-Sn alloy with 0.5µm white Cu-Sn alloy and chromium deposit plated on top.

Evaluation of these results suggest that the chromium played a significant role in protecting the substrate regardless of the underlying deposits but could not match the corrosion resistance of the nickel with chromium deposit, and therefore could not serve as a suitable alternative to the current nickel with chromium process.

The CASS results showed that the none of the alternative deposits with chromium could be a potential replacement for the nickel and chromium deposit although the white and yellow Cu-Sn alloy deposits were promising to be more corrosion resistant than the nickel deposit alone. The results suggest that chromium helps in providing corrosion protection but the underlying deposit has a larger influence to the overall corrosion protection.

Summary

Chapter 6 has presented all the experimental data collected to evaluate deposit appearance using the L*a*b* colour space. It also described surface topography using both SEM and AFM, while electrochemical corrosion resistance was evaluated using linear polarisation and EIS. The chapter also presents results on accelerated corrosion tests using NSS and CASS to give a full evaluation of each deposit.

This chapter has presented and discussed all the results obtained in this study, while also providing explanations for the conclusions drawn. Combining the results from all the different techniques used within this study the following summary was made:

‘*The white and yellow Cu-Sn alloys provide corrosion properties that have an advantage over the nickel deposit but when used in the process of plating chromium as a top coat the corrosion properties diminish, thus leaving the standard nickel and chromium process by far the best in terms of providing corrosion protection to the substrate. If corrosion protection was not primary then the 0.5µm white Cu-Sn alloy with chromium has the potential to replace the existing process but this would be limited to the application.’*

CHAPTER 7: CONCLUSION

This chapter describes the conclusions drawn from this study and also reviews the aims and objectives set out at the start of the project with a view to confirm if objectives were achieved. It also highlights the contribution to knowledge this study may have achieved.

The main aim of this research as outlined at the onset is as follows:

"to find a commercial replacement for nickel as a suitable layer under decorative trivalent chromium surface for the electroplating industry"

This aim was achieved by recommending the replacement of the nickel layer with a white Cu-Sn alloy deposit in applications where the appearance was primary, thus providing an alternative commercial process for the electroplating industry.

The key objectives of this research as outlined in Chapter one are as follows:

1. Review current commercial plated deposits that have been formulated, and evaluate the deposits.
2. Review current formulated deposits that have not been commercialised and evaluate the deposit.
3. Investigate new potential formulations which may include adaptations of additives within an existing process.

Objective 1 was achieved by the current commercial deposits being fully reviewed and evaluated within this study and concluded that the white Cu-Sn alloy deposit has a limited potential as a suitable alternative to the nickel deposit. Other commercial alternatives reviewed included palladium, tin and gold alloys, but were concluded not to have suitable properties required to meet the objectives of the study.

Objective 2 was achieved by reviewing non commercialised formulations of various cyanide free Cu-Sn alloys. It was concluded that the cyanide free Cu-Sn alloy would be of value as a non-toxic process but however, was found not to be beneficial because the electrolytes were unstable.

Objective 3 was achieved by using an existing commercial process known as Starvet (white Cu-Sn alloy) and plating the deposit to an increased thickness. The conclusion was that it was not practical, and therefore the study explored the use of an additional yellow Cu-Sn alloy deposit. Combining the white and yellow Cu-Sn alloy deposits as a duplex system enabled a thicker deposit which was evaluated.

To achieve the following objectives:

- The compatibility with trivalent chromium as opposed to hexavalent chromium.
- Its ability to fit within an existing plating line.
- The finished surface must show equivalent L*a*b* colour values, hardness, toughness and adherence characteristics.
- The corrosion protection must be at least equivalent to that of nickel and chromium.

- The chemicals used must not be more harmful or aggressive than the existing solutions used today, including the final deposit.
- Process control must not be more labour intensive than the existing nickel electrolyte, and therefore not increase the process cost.
- The deposition rate must be similar to that of nickel.
- The cost of the process must not be more than the nickel process.

The above mentioned objectives were achieved as follows:

- The yellow and white Cu-Sn alloy deposits were compatible with the trivalent chromium and could be incorporated within an existing plating line without increasing labour costs.

- Evaluation of the yellow and white Cu-Sn alloy deposit underwent both colour and topography analysis using spectrophotometry, scanning electron microscopy and atomic force microscopy. The corrosion resistance of the deposit was evaluated using electrochemical techniques (linear polarisation and electrochemical impedance spectroscopy) and accelerated corrosion salt spray tests (neutral salt spray and copper accelerated acetic acid salt spray).

- Both the yellow and white Cu-Sn alloys are not known allergens unlike the nickel deposit, therefore they are less harmful to the public. Commercially the yellow and white Cu-Sn alloys are used as a cheaper alternative to nickel in other applications and therefore the process costs are acceptable to the electroplating industry.

The conclusions derived from this study on the evaluation of the white Cu-Sn alloy and the duplex yellow with white Cu-Sn alloy processes as a replacement for the nickel layer under decorative chromium are as follows:

- An experiment was carried out to determine the colour of the deposits using a spectrophotometer, the results were recorded using the L*a*b* colour space. This study identified that the 0.5µm white Cu-Sn alloy plated with chromium matched the appearance of the nickel with chromium deposit and therefore could serve as a potential alternative based on appearance. Without the chromium deposit the 0.5µm Cu-Sn alloy was lighter and bluer, thus noticeably different from the nickel.

- The spectrophotometer results showed that the 2.0µm white Cu-Sn alloy with chromium deposit and the 4µm, 12µm and 24µm yellow Cu-Sn alloy also with chromium deposits were significantly different in appearance from the standard nickel with chromium deposit, and therefore would not be suitable alternatives based on their appearance compared to the standard nickel with chromium deposit.

- An experiment was carried out to characterise the topography of the deposits using a scanning electron microscope (SEM). The results identified a slight difference in topography between the 0.5µm and 2.0µm white Cu-Sn alloy with chromium deposit compared to the nickel with chromium deposit. The difference appeared to show an increase in nodulations with the white Cu-Sn alloy deposit, this characteristic influenced the chromium deposit as increased

nodulations were visible. It was therefore concluded that the difference could explain the background haze that was noticeable with the 2.0µm Cu-Sn alloy but not with the nickel deposit. No visible signs of pitting or other defects could be identified to suggest that the increased nodulations could hinder the corrosion resistance of the deposit, therefore the white Cu-Sn alloy was still considered as a potential alternative to the nickel deposit.

- The SEM images of the 4µm, 12µm and 24µm yellow Cu-Sn alloy with chromium deposits was identified as having a different topography from the nickel with chromium deposit. The crystalline topography of the yellow Cu-Sn alloys could mean that the deposits would have an increased surface area compared to the smoother nickel deposit. Although the chromium appears to smooth out the topography of the yellow Cu-Sn alloys, it would still have an increased surface area. It is not visible from the SEM images but there is the potential for corrosion to start more easily in the recesses of the crystalline structure.

- An experiment was carried out to determine the roughness of the deposit under test by using an atomic force microscope (AFM). The results confirmed that the 0.5µm white Cu-Sn alloy with chromium deposit had a similar roughness structure to the nickel with chromium deposit with no defects on the deposit to affect the corrosion protection. The SEM identified a similar deposit structure, and therefore suggested that the 0.5µm white Cu-Sn alloy deposit would reflect light in a similar way to the nickel deposit. The results also indicate that the 2.0µm Cu-Sn alloy has increased surface roughness, which confirms the theory

that the light reflected off the surface would be different compared to those of 0.5µm white Cu-Sn alloy and the nickel deposits. This being a plausible reason for the background haze visible in the 2.0µm white Cu-Sn alloy deposit.

- The AFM results clearly identified the 4µm, 12µm and 24µm yellow Cu-Sn alloy with chromium deposit to have increased roughness compared to the nickel with chromium deposit. The AFM results support the SEM data to confirm that the yellow Cu-Sn alloy has a different deposit structure compared to the nickel deposit. The visible dull deposit can be explained in terms of the light being reflected differently and also due to increased roughness.

- An experiment was carried out to investigate the corrosion protection of the deposits under test by using the neutral salt spray (NSS) accelerated corrosion test. The results confirmed that the 0.5µm and 2.0µm white Cu-Sn alloy had slower corrosion rate compared to the nickel deposit. However, when chromium was plated on top, the corrosion protection of the white Cu-Sn alloy was reduced and the nickel with chromium deposit clearly offered more corrosion protection. This shows that the electrochemical corrosion pattern of the chromium and underlying deposit have an influence on the overall corrosion resistance of the deposit. If this was not the case the expectation would have been that the chromium remained consistent regardless of the substrate. Therefore, NSS results would show the white Cu-Sn alloy with chromium deposit to be more corrosion resistant than the nickel with chromium, but this is not representative of the results obtained in this study.

- The NSS accelerated corrosion test showed that the duplex Cu-Sn alloy (white and yellow combined) with and without chromium as a top coat had a faster corrosion rate than the nickel with chromium deposit, thus confirming that it is not a suitable alternative to the nickel deposit. The aim of the duplex Cu-Sn alloy was to plate a thicker deposit using the yellow Cu-Sn alloy to stop any issue of porosity with a thin deposit, then followed by the white Cu-Sn alloy deposit plated to provide the required appearance. If the white Cu-Sn alloy was plated thicker, the appearance would be compromised as shown by the L*a*b* values for the 2.0µm white Cu-Sn alloy deposit.

- NSS accelerated corrosion test showed that increasing the thickness of yellow Cu-Sn alloy reduced the corrosion protection in comparison to using the white Cu-Sn alloy, therefore suggesting that the porosity of the deposit was not the major factor, but the alloy composition of the deposit was also an influence.

- An experiment was carried out to investigate the corrosion resistance of the deposits under test by using the copper accelerated acetic acid salt spray (CASS) corrosion test. The results showed that both the 0.5µm and 2.0µm white Cu-Sn alloy had slightly better corrosion protection to the nickel, but when chromium was electroplated on top, the nickel with chromium offered the best corrosion protection overall. These results support the NSS corrosion test carried out, and therefore it can be concluded in terms of corrosion resistance that the white Cu-Sn alloy could not replace the nickel deposit for applications requiring any significant corrosion resistance.

- CASS corrosion test also showed that the 4µm, 12µm and 24µm yellow Cu-Sn alloy with and without chromium did not offer the same level of corrosion protection as the nickel deposit with and without chromium. These results were supported by the NSS corrosion test and from this it can be concluded that the yellow Cu-Sn alloy plated as a duplex process did not improve the corrosion resistance and therefore would not be a suitable replacement for the nickel deposit.

- An experiment was carried out to determine the electrochemical corrosion resistance using linear polarisation. The results from this study show that the 0.5µm and 2.0µm white Cu-Sn alloy have slower corrosion rate compared to the nickel deposit as evident from the higher polarisation resistance values obtained. When chromium was used as a topcoat, the corrosion protection for both deposits was recorded to be less than that for the nickel with chromium. This is supported by the results observed in the accelerated corrosion tests where the polarisation resistance was significantly higher for the white Cu-Sn alloy deposits compared to the nickel. Based on the linear polarisation results the white Cu-Sn alloy deposit would be expected to have more corrosion resistance for the accelerated corrosion tests, but this was not observed. An explanation as to why this was not the case could be due to the limitations of the electrochemical test (the porosity of a deposit and the small area of the panel tested). The electrochemical tests cannot identify all the imperfections in a deposit where the accelerated corrosion tests would start to corrode first.

- The linear polarisation tests showed that the 4µm, 12µm and 24µm yellow Cu-Sn alloy with and without chromium have very high corrosion rates compared to the nickel deposit, this was supported by the accelerated corrosion tests carried out in this study. Although the yellow Cu-Sn alloy was plated thicker to reduce the porosity of the deposit, the high percentage of copper in the alloy may have decreased the corrosion resistance, making it unsuitable as a replacement for nickel.

- The calculated corrosion rate using the linear polarisation technique show that none of the alternative deposits proposed would offer the same corrosion protection as the nickel with chromium deposit. In spite of the assumptions made in this calculation, the accelerated corrosion tests supported the linear polarisation results by also demonstrating that the corrosion performance of the nickel with chromium could not be matched by any of the alternatives tested in this study.

- An experiment was carried out to determine the resistance and capacitance of the deposit to provide further information on the corrosion behaviour of each deposit by using electrochemical impedance spectroscopy (EIS) technique. This study found that the data fitted a two time constant equivalent circuit and as expected, metallic corrosion took place at one of the time constants. The second time constant was more difficult to explain since results did not fit with further metallic corrosion or formation of an oxide layer as expected. Further investigation into the coating properties was beyond the scope of this study and therefore it was not possible to provide a full explanation into the EIS data.

Contribution to Knowledge

This study has contributed to knowledge by systematically evaluating several potential processes that could serve as alternatives to the nickel deposit in a commercial plating process used with a decorative chromium finish. The white Cu-Sn alloy can be used in replacement of nickel for applications where appearance is primary. In such a scenario the risk of exposure to allergic contact dermatitis and possible carcinogenic effects associated with the nickel deposition process could be minimised or eliminated entirely.

The white Cu-Sn alloy has limitations and cannot replace the nickel deposit in all applications due to inability to provide corrosion protection. The option of a duplex Cu-Sn alloy system also proved inadequate due to the dull appearance and poor corrosion resistance when compared to the standard nickel process. As a consequence both the white and yellow Cu-Sn alloys could not be recommended as a suitable replacement for all the applications that use the nickel deposit.

The commercial formulation of the white Cu-Sn alloy uses the toxic chemical sodium cyanide, although this study had reviewed the non cyanide formulations it was concluded that the instability of the electrolytes rendered it unsuitable as a practical alternative to the existing nickel process.

Summary

The conclusions made in this chapter are based on the data collected for the experiments and carried out in this study. Results showed that the standard nickel with chromium deposit could be replaced by the 0.5µm white Cu-Sn alloy with

chromium deposit for applications where appearance only is primary and little corrosion protection is necessary. For applications that require corrosion protection no suitable alternative was found to replace the nickel deposit and therefore it was concluded that for the majority of applications that used the nickel with chromium deposit, there was no suitable alternative evaluated during this study. The contribution to knowledge from this study is the elimination of the risk of allergic contact dermatitis in specific applications where white Cu-Sn alloy is a suitable replacement for the nickel deposit.

The novelty of this study is that even though there is a current search for a suitable replacement for nickel and its compounds in the light of their reclassification as health hazards, there is no report till date describing the approach in its entirety, adopted in this study. It is therefore hoped that future researchers would not need to go through this route again in the search for a suitable replacement for nickel under chromium plating.

CHAPTER 8: FURTHER WORK

This chapter will make suggestions for further work that can be carried out to either improve upon the work carried out in this study or explore an alternative approach that has not been investigated.

- This study focused mainly on the Cu-Sn alloy as a replacement for nickel under decorative chromium, the electrolyte used was cyanide based suitable for a stable commercial process. The cyanide free Cu-Sn alloy electrolytes have been shown to produce deposits with success but due to the stability issues of the electrolyte over a relatively short period of time, it has not become a commercial process. Further work into producing a more stable electrolyte that is cyanide free would prove beneficial to the electroplating industry in terms of health and safety not only to improve this study but as a process in its own right.

- The white Cu-Sn alloy deposit was identified as an alternative to the nickel deposit where the appearance was primary. This was due to the deposit being thin and relying on the levelling and brightness of the copper deposit underneath. Further work to produce a thicker white Cu-Sn alloy that remained level and bright, could have the potential to provide a more corrosion resistant deposit, based on the NSS and CASS accelerated corrosion test results obtained in this study.

- The yellow Cu-Sn alloy was not as corrosion resistant as the white Cu-Sn alloy although the deposit was plated thicker to minimise porosity. Further work to investigate how the alloy composition improves the corrosion resistance including the grain size and crystallinity could provide valuable information on improving the work carried out in this study.

- The EIS work carried out within this study could not identify all aspects of the surface characteristics of the deposits. It appeared that metallic corrosion was taking place in the higher frequency area while another activity that was not typical of an oxide layer formation or metallic corrosion took place in the lower frequency area. Further work to clarify what is happening would provide more information and understanding to move this study forward.

- Further work into a new approach to finding other alternative deposits to nickel and chromium could mean a completely new thinking and not just the replacement of the nickel layer. All aspects however would need thorough investigation in terms of corrosion resistance, appearance and abrasion testing to give a few examples.

- This study focused on the electroplating technique typical to the nickel with chromium process, this method was chosen so that if any alternatives were identified it would be possible to work with the existing plating line used in commercial production and therefore could be compatible with other electrolytes already in use. Further work into other plating techniques could be investigated for example ionic plating, electroless plating and pulse

plating. By changing the technique other chemicals could be used that were not feasible as an electrolyte for electroplating.

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APPENDIX 1

Publication 1

Authors	Stacey Handy, Prof Chike F Oduoza and Dr Trevor Pearson
Year	2006
Title	Theoretical aspects of electrodeposition of decorative chromium from trivalent electrolytes and corrosion rate study of different nickel/chromium coatings.
Journal	Transaction of the institute of metal finishing
Volume	84
Number	6

Theoretical aspects of electrodeposition of decorative chromium from trivalent electrolytes and corrosion rate study of different nickel/chromium coatings

S. L. Handy[1], C. F. Oduoza[2] and T. Pearson*[3]

The present paper presents a review of theoretical aspects of deposition of chromium from trivalent chromium electrolytes and a corrosion rate study of the initial rate of corrosion of chromium deposits from these electrolytes on nickel deposits. A higher rate of corrosion was obtained from chromium deposits plated from a chloride based electrolyte as compared with a sulphate based electrolyte. No significant difference in corrosion rate was observed when comparing deposits plated from a sulphate based electrolyte with deposits obtained from a standard hexavalent chromium electrolyte.

Keywords:

Introduction

Electrodeposited chromium has unique properties which make it extremely useful as a final coating on many items. It has a high degree of hardness (850–1100 HV) and has a high level of brightness as deposited combined with an attractive blue/white appearance.[1] X-ray diffraction studies on the deposit show a high degree of preferred orientation which tends to produce a high level of tensile stress within the deposit leading to spontaneous cracking of thicker deposits.[2] This cracked deposit can improve the oil retention properties of thicker deposits and this has many engineering applications in lubricated wear situations, while in decorative applications, microdiscontinuous chromium deposits can spread the corrosion current in a corrosive environment thus improving corrosion performance.[1]

For many years, chromium has been deposited from electrolytes based on chromic acid where the chromium is in a hexavalent oxidation state. It has been recognised since the inception of industrial chromium plating that the use of chromic acid presents many hazards in terms of the chemical reactivity and toxicity of the chromium plating bath. Also, there are several well known technical difficulties experienced in the deposition of chromium from chromic acid electrolytes. These have been summarised by Smart *et al.*[3] as follows:

(i) very low efficiency with 75–85% of the applied current being used for the discharge of hydrogen
(ii) the need for high average cathode current densities, generally of the order 10–15 A dm^{-2}
(iii) poor covering power: not only poor coverage in low current density areas but also around holes and slots, i.e. 'chrome blows'
(iv) 'burning', i.e. grey deposits in high current density areas
(v) poor 'throwing power': the poor metal distribution resulting in thick electrodesposits on the edges and protruding parts of cathodes and thin deposits in recesses, with the ratio between the maximum and minimum being worse than any other electroplated metal
(vi) interruption of the current during electroplating produces 'milky' deposits, i.e. 'white washing'
(vii) solid chromic acid and its strong solutions have immediate detrimental effects on human tissue, burning the skin, particularly the eyes, but even dilute solutions have the insidious effect of causing ulcers, either from splashes or inhalation of spray
(viii) chromic acid is a strong oxidising agent and so is a potential fire hazard, being able to ignite paper and wood
(ix) high metal concentrations, i.e. 130 g L^{-1} chromium metal in a typical 250 g L^{-1} chromic acid solution
(x) need for a chemical reduction process during effluent treatment to reduce Cr(VI) to Cr(III); also a sludge problem after alkali neutralisation owing to its high metal concentration, for example twice as much as in a standard nickel plating bath.

In addition to these problems, chromic acid is now classified as a carcinogen and is subject to increasingly stringent exposure and discharge controls.

[1]School of Engineering and Built Environment, University of Wolverhampton, City Campus, WV1 1SB, UK
[2]School of Engineering and Built Environment, University of Wolverhampton, Telford Campus, TF2 9NT, UK
[3]MacDermid PLC, Birmingham B9 4EU, UK

*Corresponding author, email tpearson@macdermid.com

Published by Maney on behalf of the Institute
Received
DOI 10.1179/174591906X130275

Because of the problems associated with the electrodeposition of chromium from hexavalent electrolytes, a considerable amount of research effort has been directed at producing commercially acceptable chromium plating baths based on trivalent chromium. Because trivalent chromium is the stable state for chromium ions, these baths are much less reactive than hexavalent baths and thus much safer to use. The first company to patent a workable trivalent chromium based bath was Albright and Wilson who filed a patent in 1974 for a bath based on chromium chloride, boric acid, ammonium chloride and bromide ions.[4] Shortly after that (in 1975), IBM produced an electrolyte based on chromium sulphate and thiocyanate using a divided cell arrangement to prevent anodic oxidation of trivalent chromium.[5] Further research by both companies produced a considerable number of patents of improvement.[6–20] Cannings worked with the IBM process in a collaborative project and produced their own patent which was filed in 1982.[21] In spite of this considerable amount of research and development by major companies, till now only decorative processes capable of producing thin deposits are commercially available and the uptake of these processes within the industry has been slow. The main reason for this is the intolerance of trivalent baths to impurities and metallic contamination. However, legislation is likely to eventually force most electroplaters to seriously consider the use of trivalent processes. It is the aim of the present paper to consider in detail the electrochemical and chemical processes that occur during deposition from trivalent electrolytes, and also to compare the corrosion rate of different nickel/chromium coatings in order to assess whether the use of coatings applied from trivalent electrolytes has significantly different I_{corr} values compared with coatings from hexavalent processes.

Theoretical aspects of electrodeposition from trivalent chromium electrolytes

Thermodynamic considerations

The standard reduction potential for trivalent chromium ions is as follows[22]

$$Cr^{3+} + 3e^- \rightarrow Cr^0 \quad E^0 = -0{\cdot}744V$$

At first sight, it appears that it should be relatively easy to deposit chromium from a trivalent electrolyte because zinc reduction has an E^0 value of $-0{\cdot}76$ V and this can readily be achieved in practice. However, whereas in zinc plating reduction of zinc to metal is the only available electron transfer reaction, with trivalent chromium, it is possible to transfer one electron to form divalent chromium

$$Cr^{3+} + e^- \rightarrow Cr^{2+} \quad E^0 = -0{\cdot}407V$$

This process occurs at a much lower negative potential than reduction of chromium(III) to metallic chromium and so would be expected to occur preferentially. Finally, deposition of chromium metal from chromium(II) ions occurs at a much higher negative potential

$$Cr^{2+} + 2e^- \rightarrow Cr^0 \quad E^0 = -0{\cdot}913V$$

Thus it would be expected that the predominant reaction during deposition would be the transfer of one electron to form divalent chromium. Chromium would not be deposited from the divalent chromium ions owing to the highly negative reduction potential but because divalent chromium is strongly reducing, the following reaction would occur

$$2Cr^{2+} + 2H^+ \rightarrow 2Cr^{3+} + H_2$$

Thus the net reaction process would be expected to produce hydrogen rather than chromium metal.

This discussion illustrates only what would be expected from a thermodynamic point of view. However, because that a process is thermodynamically favoured does not mean it will happen in practice since it is the kinetics of the reaction which determines the rate. Therefore, if reduction from trivalent chromium to metal is kinetically favoured compared with the reduction to divalent chromium, then this may be the predominant reaction. Also, in practical plating solutions, complexation of ions may shift equilibrium potentials considerably from the E^0 values quoted above (in a negative direction).

Kinetic considerations

Ligand exchange rate

Ligand exchange rate has been considered by Smart *et al.*[3] They compared literature values for first order rate constant for exchange of water ligands between nickel complexes and chromium complexes as follows.

The $[Cr(H_2O)_6]^{3+}$ ion is a very stable species. The amount of time that a water molecule spends in the coordination sphere, 'mean residence time', can be several hours. While other metals coordinate with water molecules, these latter usually exchange rapidly between the solvent and the complex, for example as in nickel solutions

$$[Ni(H_2O)_6]^{2+} + H_2O^* \rightarrow [Ni(H_2O)_5(H_2O^*)]^{2+} + H_2O$$

The first order rate constant for the above reaction is 4×10^4, signifying rapid interchange. The same interchange takes place for Cr(III)

$$[Cr(H_2O)_6]^{3+} + H_2O^* \rightarrow [Cr(H_2O)_5(H_2O^*)]^{3+} + H_2O$$

where * denotes molecule originally in solvent.

However, for this reaction the first order rate constant is 5×10^{-7}. A very slow exchange thus takes place owing to the kinetic inertness of the Cr(III) species.

This explains some of the difficulties encountered in depositing chromium from a trivalent electrolyte. It appears from the above that the combination of slow ligand exchange combined with unfavourable reduction potentials will make deposition of chromium from a trivalent electrolyte problematic.

Formation of oligomeric and polymeric olated species

In addition to the slow ligand exchange processes, trivalent chromium has the property of forming short or longer chain polymers by bridging via a water ligand and subsequent elimination of H^+. This process is illustrated in Fig. 1.

The tendency to form olated species increases as the pH of the electrolyte increases. Watson *et al.*[23–26] postulated that the presence of divalent chromium accelerated both ligand exchange kinetics and the rate of formation of olated species, particularly within the

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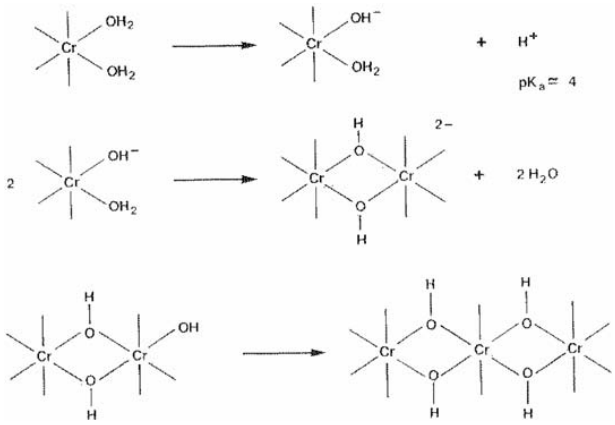

1 Olation of chromium(III) species (after Watson *et al.*)

diffusion layer during electrodeposition. This was used to explain the lack of sustained chromium deposition during trivalent chromium plating because the olated species would not be expected to be electroactive.[23–25]

pH of diffusion layer and chromium concentration – mass transport

The pH of the diffusion layer is of great importance in all electrodeposition processes, and particularly so in the case of deposition from trivalent chromium electrolytes. Watson *et al.*[24,25] measured the pH of the diffusion layer by using the Brenner drainage technique[27] using microelectrodes. They found that under conditions of normal operation, the diffusion layer pH tended to stabilise ~ 4 from electrolytes with a bulk pH 2·5 (a citrate based bath). A glycine electrolyte with a bulk pH 1·8 was found to have a diffusion layer pH 2·5. In both cases, the increase in pH was $\sim 1{\cdot}5$ units from the bulk pH.

The Brenner drainage technique relies on the electrolyte with a relatively low viscosity within the diffusion layer in order to work effectively. It is possible that in the case of trivalent chromium electrolytes, a considerable viscosity increase occurs within the diffusion layer owing to olation reactions. It would be preferable to use another technique for modelling diffusion layer pH.

During the electrodeposition process, at least 90% of the current is used to generate hydrogen. As the bulk pH of a decorative electrolyte is in the region of 2·5–3·5, the hydrogen ion activity is between 0·0003 and 0·003M. This is far too low a concentration of hydrogen ions to allow the passage of the full plating current. The bulk of the hydrogen discharge therefore comes from the direct reduction of water

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$

The molarity of water in a typical plating bath is ~ 50M so the hydrogen evolution reaction is unlikely to become diffusion limited. The reduction of water content at the diffusion layer interface can be calculated (if the diffusion coefficient of water and thickness of the diffusion layer are known), and hence the concentration of hydroxide ions at the surface can be deduced by subtraction.

In order to determine the surface concentration of species in non-steady state diffusion, Fick's second law[28] can be used

$$\frac{dC}{dt} = \frac{d^2C}{dx^2} \quad (1)$$

where C is the concentration of the diffusing species, x is the distance from the cathode and t is the time. In considering non-steady state diffusion in convective systems, if a diffusion layer of finite thickness is formed, then the boundary conditions for solving the equation are

$$C = C_b \quad x \geq 0 \text{ and } t = 0$$

$$C = C_b \quad x \geq \delta \text{ and } t > 0$$

$$\frac{dC}{dx} = \frac{j}{zFD} \quad x = 0 \text{ and } t > 0$$

Rosebrugh and Miller[29] obtained a solution to equation (1) subject to the above boundary conditions by the use of a Fourier transformation. They determined that the surface concentration of diffusing species under conditions of both convection and diffusion could be written as

$$C_s = C_b - \frac{j\delta}{zFD}k \quad (2)$$

where C_s is the surface concentration, C_b is the bulk concentration, j is the current density, δ is the thickness of the diffusion layer, z is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient and k is a constant given by the following equation

$$k = 1 - \frac{8}{\pi^2}\sum_{n=1}^{n=\infty}\frac{1}{(2n-1)^2}\exp\left\{-\left[(2n-1)^2\frac{\pi^2 Dt}{4\delta^2}\right]\right\} \quad (3)$$

where n is any integer.

Siver[30] showed that for small values of t and large values of δ, i.e. $Dt/\delta^2 < 0{\cdot}1$, k was given by the following equation

$$k = \frac{2}{\pi^{1/2}}\left(\frac{Dt}{\delta^2}\right)^{1/2} \quad (4)$$

whereas for larger values of t and small values of δ, i.e. $Dt/\delta^2 > 0{\cdot}1$

$$k = 1 - \frac{8}{\pi^2}\exp\left(-\frac{\pi^2 Dt}{4\delta^2}\right) \quad (5)$$

Using this computational method, the hydroxide ion concentration was estimated for a typical trivalent electrolyte. The diffusion coefficient for water was estimated using an empirical equation developed by the US EPA[31]

$$D = 0{\cdot}00022 MW^{-2/3} \quad (6)$$

where D is the diffusion coefficient ($cm^2\ s^{-1}$) and MW is the molecular weight of the diffusing species.

The diffusion layer thickness in electroplating solutions typically varies between 10 and 20 μm[32] so a nominal value of 15 μm was used for the computation. The computation was performed at different current densities and yielded the values as shown in Table 1.

To model the effect of this concentration of hydroxide ions on the diffusion layer pH, this quantity of sodium hydroxide was added to a working solution of the plating solution and a solution of the buffer salts and measuring the pH in each case. The results of this experiment are plotted in Fig. 2.

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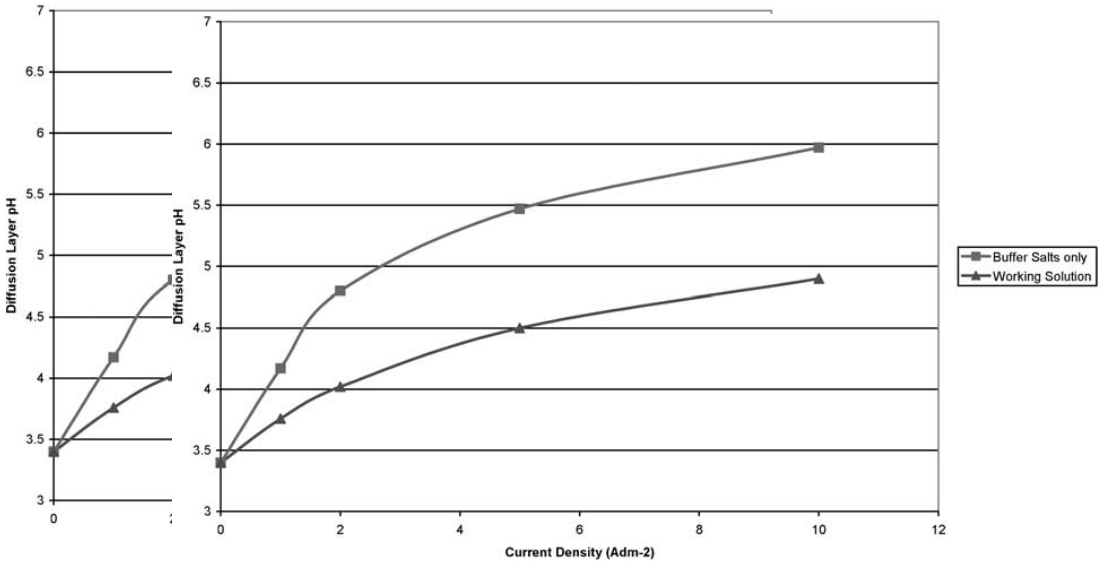

2 Estimated diffusion layer pH at different current densities in trivalent chromium electrolyte

It can be seen from the above figure that the pH rise produced in the case of the full working solution was 1·5 units at 10 A dm^{-2} which is the same pH rise as was detected in the work carried out by Watson *et al.*[24,25] However, when the same experiment was carried out using just the buffer salts for the process, a much larger pH change was produced. This indicates that a substantial amount of buffering is carried out by the chromium species themselves and this must lead to a change in the composition of the chromium complexes within the diffusion layer. This could be the reason why the deposition rate of chrome falls as plating progresses.

In addition to the pH change in the diffusion layer, depletion of chromium must be considered. Some decorative trivalent chromium plating processes operate at chromium concentrations as low as 0·1M and also operate at current densities up to 10 A dm^{-2}. The computational method used to calculate the hydroxide concentration at the cathode interface can also be used to calculate depletion of chromium provided that the cathode current efficiency of the process is known. As stated earlier, most decorative processes operate with a cathode efficiency of $<10\%$ so for the calculation, an efficiency was chosen. Another problem with the calculation for the chromium is with the estimation of the diffusion coefficient since the speciation of the electroactive chromium ions is unknown. For the purpose of illustration, a diffusion coefficient was calculated based on a 1:1 malic acid complex of chromium. Although this is unlikely to be the electroactive species in practice, the molecular weight would have to be substantially higher to make a large difference to the calculated diffusion coefficient.

Table 1 Calculated hydroxide ion concentration generated in diffusion layer during electrolysis of trivalent electrolyte

Current density, A dm^{-2}	Hydroxide ion concentration, M
1	0·005
2	0·01
5	0·025
10	0·05

The results of the above simulation are shown in Fig. 3. It can be seen from this figure that the concentration of chromium would not be expected to drop $<90\%$ of the original concentration.

This illustrates that bulk chromium depletion in trivalent electrolytes is unlikely to be significant at the low cathode efficiencies achieved. However, the electroactive reducible chromium may be present in much smaller quantities than the bulk concentration.

Anode reactions

So far, only cathode reactions have been considered. It is also necessary to consider the anode reactions.

Anode reactions in chloride based electrolytes

Chloride based trivalent chromium electrolytes usually use graphite anodes directly immersed in the electrolyte. These electrolytes also may contain Bromide ions.[4] The standard potentials for the reactions involved are as follows

$$2Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \quad E^0 = 1{\cdot}33V \quad (7)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E^0 = 1{\cdot}23V \quad (8)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad E^0 = 1{\cdot}36V \quad (9)$$

$$2Br^- \rightarrow Br_2 + 2e^- \quad E^0 = 1{\cdot}06V \quad (10)$$

In practice, in the absence of bromide, the predominant reaction when graphite anodes are used is oxidation of chloride to chlorine. The relatively high oxygen overpotential raises the actual discharge potential of oxygen above that of chlorine. In the presence of bromide ions, oxidation of bromide to bromine is the preferred reaction, which then reacts further with oxidisable compounds in the electrolyte to reform bromide ions. Reaction (7), leading to the formation of hexavalent chromium does not occur to an appreciable degree in chloride based electrolytes.

Sulphate based electrolytes

These electrolytes do not contain either chloride or bromide ions so only reactions (7) and (8) can occur. Using graphite anodes, large amounts of hexavalent

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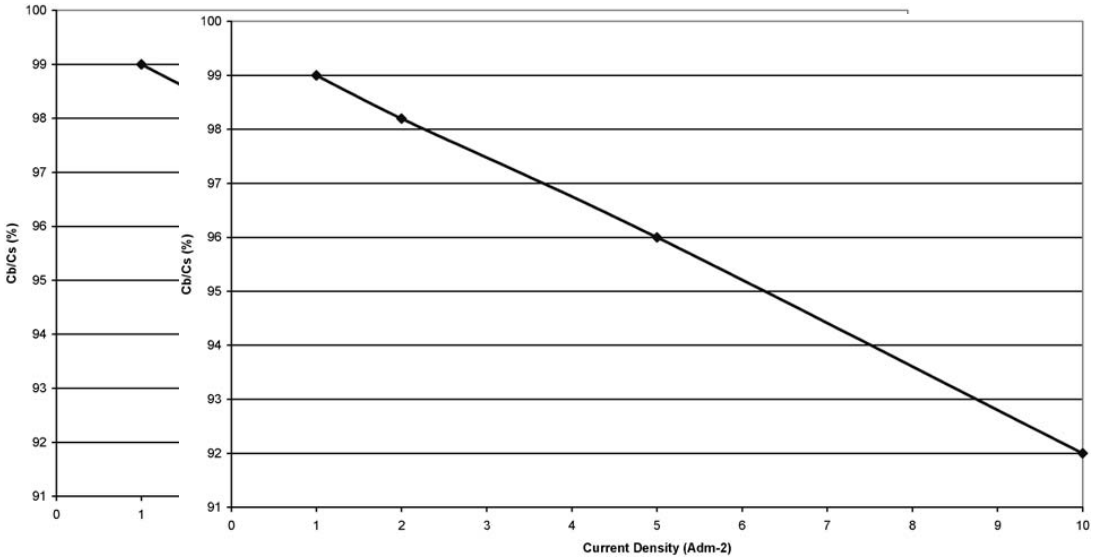


3 Calculated depletion of chromium at cathode interface from electrolyte containing 0·1M Cr and having cathode efficiency of 10%

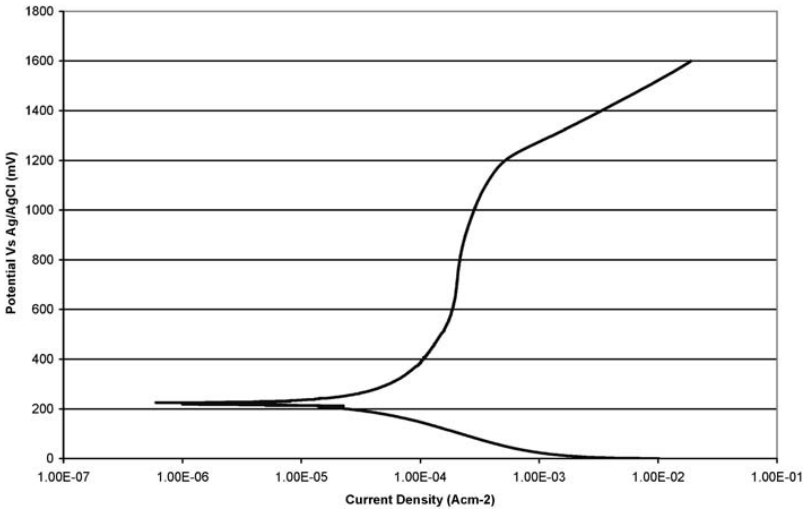
chromium are generated in the electrolyte owing to reaction (7). In early versions of sulphate catalysed electrolytes, divided cell anodes were used with a perfluorinated membrane in order to physically prevent contact of the trivalent chromium compounds with the lead anodes that were used in the process. This proved to be expensive and difficult to maintain, so the anodes currently used for this type of process are iridium/tantalum oxide coated anodes which have a low oxygen overpotential, thus favouring oxygen production rather than hexavalent chromium generation. These anodes can be used directly in the plating bath and do not require separation from the plating bath by a membrane. Figure 4 shows a typical polarisation curve for one of these anodes in a working bath.

It can be seen from this graph that the anode is essentially passive up to a potential of 1200 mV and above this point, the current increases quickly. A typical working current density of 4–6 A dm^{-2} corresponds to an anode potential of 1540 mV. Thermodynamically, this potential is high enough to oxidise chromium via reaction (7), but in practice, this tends not to be a problem. This indicates that reaction (7) tends not to be kinetically favoured on iridium oxide coated anodes.

In summary, it can be seen that from a theoretical point of view, there are many technical difficulties to overcome. In spite of this, there are workable commercial processes available which produce excellent results for decorative deposition. Corrosion performance is an important aspect of decorative nickel/chromium deposits and the next section of the present paper compares corrosion rates of chromium deposits from trivalent and hexavalent electrolytes when deposited onto various nickel undercoats.

Comparative corrosion performance of chromium electrodeposits on nickel

This section compares the I_{corr} values of chromium deposits from trivalent and hexavalent chromium processes when plated onto deposits of bright nickel and duplex/microporous nickel. These values were obtained using linear polarisation techniques. A scanning electron microscope (SEM) was used to produce



4 Polarisation curve for iridium oxide coated anode in trivalent chromium plating electrolyte

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surface images of the different chromium deposits after 48 h in 5% neutral salt spray.

Experimental details

Electroplating sequence

The following sequence was used to prepare brass panels with various coating combinations in order to compare corrosion rates.

(i) cleaning of substrate
(ii) rinse
(iii) electrodeposition of nickel
(iv) rinse
(v) electrodeposition of chromium
(vi) rinse
(vii) dry.

Following the cleaning stages, nickel was applied using one of the following combinations of deposit:

(i) bright nickel deposit from a commercial process (Lumax, MacDermid PLC)
(ii) duplex nickel + microporous nickel (Niflow, Lumax, Hypore, MacDermid PLC).

A duplex nickel system[33] has a first layer in direct contact with the substrate consisting of a semibright nickel layer with a very low sulphur content. The second layer is a bright nickel layer which contains substantial amounts of sulphur owing to codeposition of sulphur containing additives (e.g. saccharin). This increases corrosion protection because the semibright nickel is more noble than the bright nickel layer which corrodes preferentially. Microporous nickel is applied as a third layer and has a thickness of ~ 1 μm, this layer contains micropores which help spread the corrosion current, thus preventing rapid local corrosion at macrodefects in the coating.

Following the application of the nickel deposit, 0·3 μm of chromium was then plated on top of the nickel using one of four solutions. These were as follows:

(i) hexavalent chromium solution (Mach 2, MacDermid PLC)
(ii) trivalent chromium solution (sulphate based solution giving a light coloured deposit) (Trimac III, MacDermid PLC)
(iii) trivalent chromium solution (sulphate based solution giving a dark coloured deposit) (Twilite, MacDermid PLC)
(iv) trivalent chromium solution (chloride based solution) based on US patent 3954574.

Brass panels (size $10 \times 7{\cdot}5 \times 0{\cdot}05$ cm) were used as the substrate and plated on both sides. A new panel was used for each plating sequence. The different combinations of both nickel and chromium used are shown below:

(i) bright nickel + trivalent chromium (sulphate based, light coloured deposit)
(ii) duplex nickel + microporous nickel + trivalent chromium (sulphate based, light coloured deposit)
(iii) bright nickel + trivalent chromium (chloride based)
(iv) duplex nickel + microporous nickel + trivalent chromium (chloride based)
(v) bright nickel + trivalent chromium (sulphate based, dark coloured deposit)
(vi) duplex nickel + microporous nickel + trivalent chromium (sulphate based, dark coloured deposit)
(vii) bright nickel + hexavalent chromium
(viii) duplex nickel + microporous nickel + hexavalent chromium

Table 2 shows the operating conditions for each chromium electroplating solution.

Linear polarisation measurements

A potentiostat (EG + G Instruments, Model 263A) was used to determine the corrosion current density I_{corr} using a linear polarisation method. This was carried out in 5% neutral sodium chloride solution using a Ag/AgCl reference electrode over a potential range of ± 20 mV versus open circuit potential. The equilibrium time that the 1 cm^2 surface of panel was in contact with the NaCl was varied (30 or 60 min).

Different factors were changed to see if they affected the corrosion rate:

(i) equilibrium time when the surface was in contact with the 5%NaCl solution (30 or 60 min)
(ii) the nickel intermediate layer (bright nickel or duplex nickel with a microporous layer)
(iii) formulation of the chromium solution (hexavalent or trivalent chromium).

Each variation was analysed five times to determine the consistency of the results. Thickness testing showed that the nickel layer either single or duplex had a final thickness of $\sim$15–23 μm and the chromium thickness between 0·2 and 0·5 μm, the thickness was measured using a fischerscope X-ray system XDL-B.

SEM examination

An SEM (Jeol model JSM-5600L V) was used to produce a surface image of the duplex nickel + microporous + chromium panels after 48 h in 5% neutral sodium chloride salt spray, Ascott model 51000. A magnification of $\times 1500$ was used in each case.

Experimental results

The mean average of the I_{corr} values using duplex nickel with microporous nickel at different equilibrium times can be seen in Table 3. Table 4 shows the mean average I_{corr} values for the bright nickel layer and different equilibrium times. All the results are shown in Fig. 5.

Table 2 Operating conditions of chromium solutions

	Hexavalent chromium[34]	Trivalent chromium[4] (chloride based)	Trivalent chromium[35] (sulphate based)	Trivalent chromium[36] (dark finish)
Total chromium metal, g L^{-1}	100–150	20–23	10–20	6–15
Temperature, °C	38–43	25–35	50–65	50–60
pH	<1	2·5–2·8	3·2–3·8	3·4–3·8
Cathodic current density, A dm^{-2}	9–15	4–10	7–15	5–10
Agitation	None	Mild air	Mild air	Mild air

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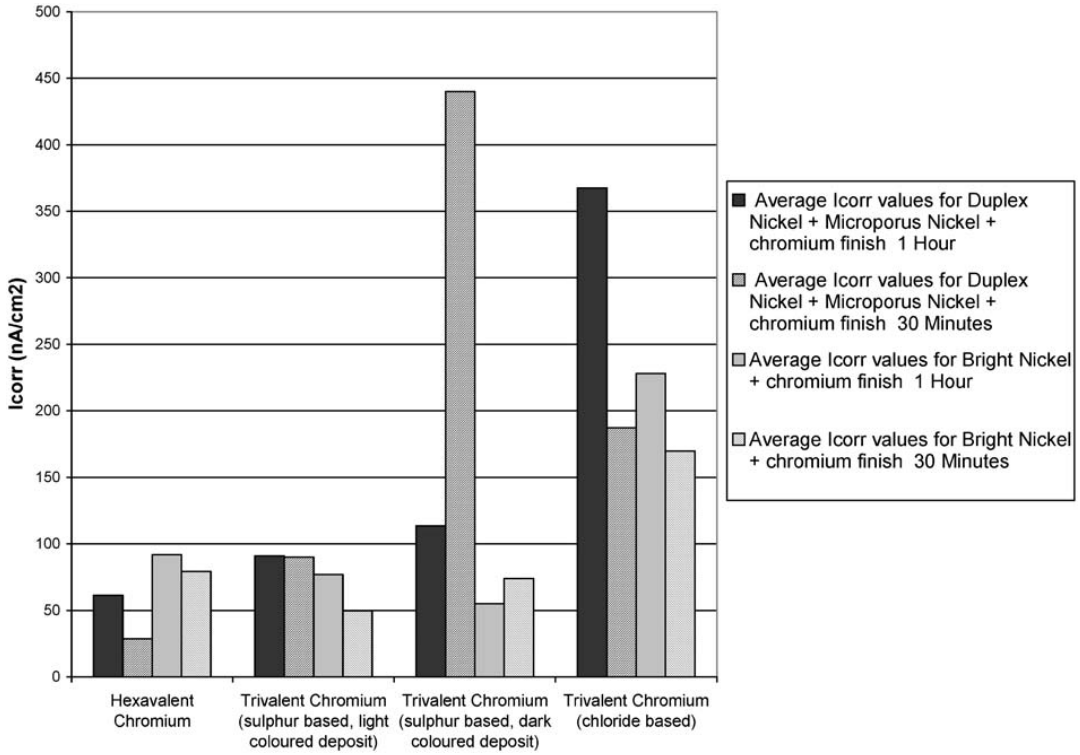

5 Mean average I_{corr} values for each set of results

Owing to the varied results a statistical analysis was carried out to see if there was any significance in the differences in the I_{corr} values. Minitab (release 13) was used to calculate the analysis of variance using a single factor general linear model. To show that the I_{corr} values from each set of results were significantly different from one another, the probability value for the null hypothesis (that all of the values were equal) had to be $<5\%$ (0·05). The results are shown in Tables 3 and 4.

Discussion of results

It can be seen that the probability value for the null hypothesis for all sets of results was $<5\%$ and therefore the results were significantly different. Further statistical analysis was carried out to see if the results showed a significant difference in I_{corr} values between the different chromium finishes. Tukey's test was used to perform this analysis.

Comparing the different bright nickel+chromium finishes with a 1 h equilibrium time showed that there was no significant difference in the I_{corr} values between the hexavalent chromium (Fig. 6), trivalent chromium (sulphate based, light coloured deposit) (Fig. 7) and trivalent chromium (sulphate based, dark coloured deposit) (Fig. 8). The trivalent chromium (chloride based) (Fig. 9) had a higher rate of corrosion compared with the other finishes. This was also the result with the bright nickel+chromium finish with a 30 min equilibrium time.

Table 3 Average I_{corr} values for duplex nickel+microporous nickel+chromium finish

	Average I_{corr} value, nA cm^{-2}	
	1 h	30 min
Hexavalent chromium	61·17	28·70
Trivalent chromium (sulphate based, light coloured deposit)	90·93	89·99
Trivalent chromium (sulphate based, dark coloured deposit)	113·6	440·0
Trivalent chromium (chloride based)	367·5	187·3
Probability value for null hypothesis	0·035	0·000

Table 4 Average I_{corr} values for bright nickel+chromium finish

	Average I_{corr} value, nA cm^{-2}	
	1 h	30 min
Hexavalent chromium	91·84	79·11
Trivalent chromium (sulphate based, light coloured deposit)	76·88	49·77
Trivalent chromium (sulphate based, dark coloured deposit)	54·98	73·90
Trivalent chromium (chloride based)	228·1	169·7
Probability value for null hypothesis	0·000	0·000

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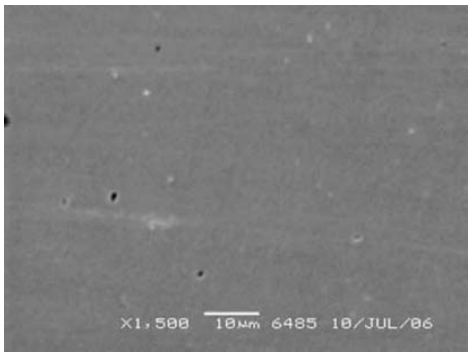


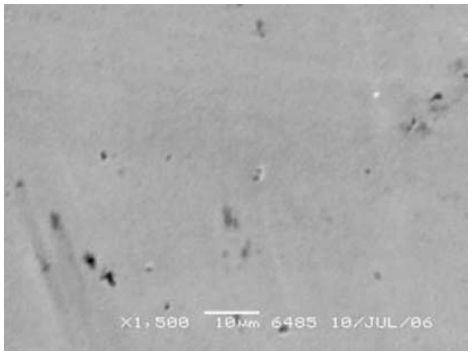
6 Duplex/microporous nickel + hexavalent chromium

Comparing duplex nickel + microporous nickel + chromium finish with a 1 h equilibrium time showed no conclusive difference between the finishes although the average I_{corr} values varied from 61·17 to 367·5 nA cm^{-2}. Comparison of the duplex nickel + microporous nickel + chromium finish with a 30 min equilibrium time showed no difference between the hexavalent chromium, trivalent chromium (sulphate based, light coloured deposit) and trivalent chromium (chloride based) processes. The trivalent chromium (sulphate based, dark coloured deposit) had a higher corrosion rate than the other chromium finishes. It is possible that a surface reaction is taking place when in contact with the 5%NaCl solution, which is complete after 1 h leading to a reduction in corrosion current.

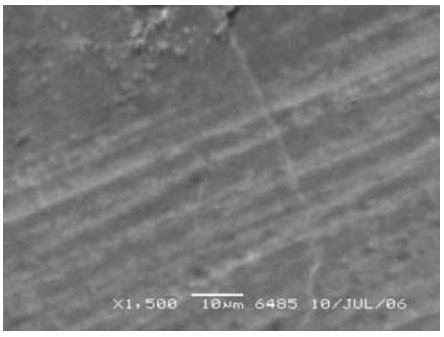
The SEM results showed the trivalent chromium (chloride based) deposit was microcracked (Fig. 9), whereas all of the other deposits were apparently crack free. This could explain the higher I_{corr} value obtained with this coating owing to increased exposure of the underlying nickel. There was little difference seen between the hexavalent chromium and trivalent chromium (sulphate based, light coloured deposit) in Figs. 6 and 7 respectively. Both of these showed isolated corrosion pores. The trivalent chromium (sulphate based, dark coloured deposit) showed a different structure of chromium compared with the other deposits, it is thought that this is due to codeposition of the sulphur.

Conclusions

1. Deposition of chromium from trivalent electrolytes is difficult owing to both thermodynamic and kinetic considerations.



7 Duplex/microporous nickel + trivalent chromium (sulphate based, light coloured deposit)



8 Duplex/microporous nickel + trivalent chromium (sulphate based, dark coloured deposit) image from SEM

2. The increases in the diffusion layer pH during electrodeposition may lead to olation of the bath causing changes in the bath composition and speciation which reduce the plating rate of the bulk electrolyte and limit the deposit thickness.

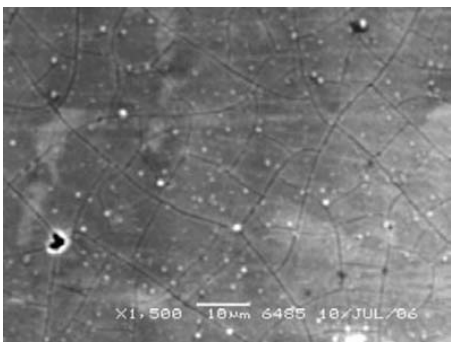
3. In spite of the relatively low chromium concentration of trivalent electrolytes, depletion of chromium within the diffusion layer is not likely to play a role in limiting plating rate or thickness.

4. I_{corr} values obtained from chromium coatings from a trivalent sulphate based electrolyte (Trimac III) on both single nickel and duplex/microporous nickel coatings were not statistically different from the values obtained from chromium coatings obtained from hexavalent baths.

5. I_{corr} values obtained from chromium coatings from a chloride based electrolyte on single and duplex/microporous nickel coatings were significantly higher than the values obtained from hexavalent baths.

6. I_{corr} values obtained from chromium coatings from a sulphate based electrolyte designed to produce dark finishes (Twilite) were significantly higher than those from a hexavalent bath when measured after 30 min immersion in the sodium chloride electrolyte. This difference became insignificant after 1 h immersion. This is possibly due to an initial surface reaction taking place owing to the high codeposited sulphur content.

7. The SEM investigation showed a similar corrosion mechanism in the case of the hexavalent chromium deposit and the light coloured trivalent chromium deposit from the sulphate bath. Deposits from the trivalent chloride based bath were microcracked.



9 Duplex/microporous nickel + trivalent chromium (chloride based)

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Acknowledgements

The authors wish to show their gratitude to the EPSRC, Kohler-Mira PLC and MacDermid PLC for the sponsorship of the present project and also MacDermid PLC for the use of their chemicals and equipment. Handy would like to thank the School of Engineering and Built Environment, University of Wolverhampton for their support during the course of the present study.

MacDermid PLC: Commercial process Twilite, MacDermid PLC, Birmingham, UK.

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Authors Queries

Journal: **Transactions of the Institute of Metal Finishing**
Paper: **84062**
Title: **Theoretical aspects of electrodeposition of decorative chromium from trivalent electrolytes and corrosion rate study of different nickel/chromium coatings**

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APPENDIX 2

Publication 2

Authors	Stacey Hingley and Prof Chike F Oduoza
Year	2011
Title	An Investigation into a Copper/Tin Alloy as an Underlying Coating to Chromium.
Journal	Journal of Materials Science and Engineering B
Volume	1
Pages	140-420

Journal of Materials Science and Engineering B 1 (2011) 410-420
Formerly part of Journal of Materials Science and Engineering, ISSN 1934-8959

An Investigation into a Copper/Tin Alloy as an Underlying Coating to Chromium

Stacey Hingley and Chike Oduoza
University of Wolverhampton, Wulfruna Street, Wolverhampton, WV1 1LY, UK

Received: December 16, 2010 / Accepted: January 07, 2011 / Published: September 25, 2011.

Abstract: The electroplating industry has been under intense pressure over the last few years due to numerous factors which include the increase in metal prices, economic climate and the new regulations. These factors have led the electroplating industry to find more economical and less harmful chemicals. The characteristics and properties of a copper-tin alloy as an alternative to the nickel deposit under chromium were investigated due to the increasing concern over health risks associated with nickel metal and its soluble salts. Spectrophotometry was used to identify the colour of the deposits by using the L*a*b* colour space. The results showed that the colour of the chromium did not change regardless of the deposit below. However, there was a colour difference between the Cu-Sn and nickel deposit, the Cu-Sn deposit was lighter, less green and more blue than the nickel deposit with the numeric values L* = 86.26, a* = 0.40 and b* = 3.25, nickel proved to be the most red and most yellow in colour with the numeric values L* = 83.12, a* = 0.81, b* = 6.68. Atomic force microscopy (AFM) characterised the surface roughness of the deposits by reporting the RMS and Rmax values. The results identified the Cu-Sn deposit to have an increased roughness to its structure with values of 8.30 nm and 73.0 nm, respectively compared to the nickel deposit with values of 3.08 nm and 18.6 nm respectively. Corrosion performance was measured by two methods, (1) electrochemical test using linear polarisation and (2) accelerated corrosion test using both neutral salt spray (NSS) and copper accelerated acetic acid salt spray (CASS). The accelerated corrosion tests identified the nickel deposit to provide better corrosion protection compared to the Cu-Sn deposit, however the electrochemical test indicated the Cu-Sn deposit with a calculated corrosion rate of 0.232 mm per year would provide better corrosion protection than the nickel deposit with a corrosion rate calculated as 0.285 mm per year. To conclude, the Cu-Sn deposit could not replace nickel in all applications but it could be used as an alternative to the nickel in applications where appearance was primary, but it would be unable to replace nickel where corrosion protection was foremost.

Key words: Cu-Sn alloy, trivalent chromium, linear polarisation, AFM.

1. Introduction

Electrodeposited nickel is widely used in many applications. A typical application is the corrosion protection it offers in conjunction with chromium plating. The reclassification of nickel and its salts to a more toxic chemical status has led the electroplating industries to research into a replacement for the nickel layer. This paper investigates if an alloy of copper and tin could be a suitable replacement for the nickel deposit under chromium. The colour, corrosion protection and surface imaging of the Cu-Sn deposit will be compared to the nickel deposit.

Corresponding author: Stacey Hingley, Ph.D., research field: electroplating. E-mail: s.l.handy@wlv.ac.uk.

1.1 Background

In 1996, an EU risk assessment was set up to investigate nickel and its compounds with regard to the effect it has on human health and also the environmental impact. EU risk assessment evaluates and sets out controls for existing substances imported into the EU when volumes exceed 10 tonnes per year. For this to happen the nickel substances in question need to be on the priority list and a Member State volunteers to act as Rapporteur. In this case, it is the Danish Environmental Protection Agency (D-EPA). There are five listed priority substances undergoing risk assessment. Since 1996 nickel metal and nickel sulphate have been on the 3rd priority list and since 2000, nickel chloride, nickel nitrate and nickel

carbonate have been on the 4th priority list.

In February 2007, there was a reclassification of the five nickel substances. Soluble nickel compounds (nickel sulphate, chloride, nitrate and carbonate) became classified as category 1 human carcinogens by inhalation (known to be carcinogenic to man), category 2 reproductive toxicants (may cause harm to the unborn child) and chronic toxicant (T; R48-23). Nickel metal became classified as category 3 carcinogen (limited evidence of a carcinogenic effect) and chronic toxicity (T; R48/23).

1.2 Review of the Health Risks Associated with Nickel and Nickel Salts

The literature provides evidence of nickel salts being carcinogenic [1-11] although not all publications support the findings. An assessment carried out by Oller in 2002 [12] found no proof that soluble nickel compounds caused cancer. What he did find was that high concentrations of soluble nickel salts could cause chronic respiratory toxicity and enhance the tumour response elicited by inhalation of carcinogens (such as cigarette smoke or insoluble nickel salts). A concern with epidemiologic studies of cancer is determining whether soluble nickel compounds have a causal or enhancing effect due to the lack of full data available. When conducting studies into nickel compounds and their carcinogenic effect, the factors that should be taken into account are: (1) Exposure limits; (2) Isolation of the person to just soluble or insoluble nickel compounds; (3) No contact with other known or suspected carcinogenic substances; (4) The health of the individual including family history of any cancers. Carcinogenic studies are difficult to conduct due to external factors that cannot be controlled. An example is the exposure to other known carcinogens such as cigarette smoke. A large proportion of the population smoke (1 in 4 people [13]) and the known carcinogenic effect of smoking and passive smoking are well known [14], so isolating the carcinogenic effect caused by nickel exposure alone becomes problematic.

Health risk associated with nickel dermatitis also known in the electroplating industry as “nickel itch” occurs when nickel salts are absorbed into the body. An allergic reaction takes place and in most cases, it can be seen in the form of a rash. Nickel allergy is one of the major factors for hand eczema; 30%-40% of people who are nickel sensitive suffer from it [15]. Different studies have found that an increase in contact time between nickel and the sweat solution increases the amount of nickel dissolved [15, 16].

1.3 Legislative and Regulating Guidance on the Use of Nickel Compounds

Controlling the risk of skin exposure to nickel and its salts within a work place can help prevent sensitisation. Less exposure to nickel reduces the risk of becoming sensitised. This can easily be done by following the COSHH (Control of Substances Hazardous to Health) regulations effective from 2002. It requires that skin exposure to nickel and its salts are prevented or adequately controlled at work. If prevention is not possible then the use of Personal Protective Equipment (PPE) is required; this would include gloves, eye protection and wearing overalls. The Health and Safety Executive (HSE) states that the role of PPE should only be used as a last resort for removing any risk to health; all other measures must be carried out first.

The public is exposed to nickel metal through everyday life. Costume jewellery uses nickel as a silver replacement to reduce costs and the clothing industry used nickel on belt buckles and buttons [17]. A person who is not sensitised to nickel would not react to these objects, but continuous contact with nickel could cause them to become sensitised. Stainless steel cutlery found in most households is not harmful to the majority of people who are sensitised to nickel because the nickel in the stainless steel is tightly bound in the alloy [17] and therefore not freely available on the surface. However there are people who are sensitised when handling stainless steel and are known to be “hyper-sensitive” to nickel [18]. In the UK, it is

thought that 30% of the population is allergic to nickel with a higher percentage of women compared to men. It is not understood if the age or sex of a person is a determinant or other factors such as culture, occupation and habits. A plausible theory for the high percentage of women being allergic to nickel is because they are more likely to come into contact through piercings and jewellery while men tend to have contact through their work [19].

The need to seek an alternative replacement for nickel in spite of its utility in the plating industry is driven by the health and safety issues concerning its use. Soluble nickel compounds account for 12%-14% of the total nickel demand [20], therefore their reclassifications mean they must undergo the authorisation procedure of REACH (Registration, Evaluation & Authorisation of Chemicals), a new law enforced from June 2007 to improve protection of human health and the environment. The chemical industry will now have greater responsibility to manage the volume of chemicals they handle and the risks the chemicals pose. Hazard information will be stored on a database and can be referred to by all concerned. REACH aims to progressively replace the more hazardous chemicals with less harmful alternatives as they are identified [21].

There are a few replacements proposed for nickel but only for a limited number of applications. A typical replacement is a copper-tin alloy called white bronze also known as speculum which has a similar appearance to silver [22]. The Cu-Sn alloy is often plated over a bright copper deposit to give a luscious finish due to the Cu-Sn alloy not having its own brightener system. Literature has shown the Cu-Sn alloy to have better corrosion resistance than nickel, and offers good wear resistance which is an advantage for the jewellery industry [23]. There appears to be no commercial alternative for the replacement of nickel when used under chromium. If the nickel can be replaced this would reduce nickel exposure to both workers in the electroplating industry and the public as a whole.

2. Experimental Procedures

2.1 Electroplating Sequence

Brass panels (size 10 × 7.5 × 0.05 cm) were prepared using a standard pre-treatment process which involved a cathodic electro-cleaner (Metex PS Activax) used at 80 ^{o}C at a current density of 0.3 amps/dm^2 for 3 min; this removed any oil and grease from the brass surface, then followed by an anodic cleaner (Metex PE E5) at 80 ^{o}C, 2 amp/dm^2 for 3 min, and then to finish the pre-treatment stage, the panels were soaked in an acid dip (Metex M-629) for 3 min to remove any oxide layers before plating. Fig. 1 shows the typical plating sequence for the standard nickel and chromium process. The panels were plated in the nickel electrolyte (NiMac Clarion II) at 55 °C at a current density of 4 amps/dm^2 for 30 min to give a deposit thickness of 20 μm. The chromium electrolyte (TriMac III) if required is then plated at 60 °C and at a current density of 10 amps/dm^2 for 12 min to give a deposit thickness of 0.3 μm.

Fig. 2 shows the plating sequence for the electrodeposition of the Cu-Sn and chromium deposits. The brass panels were plated with bright copper (CuMac Rival) at 25 °C at a current density of 3 amps/dm^2 for 30 min to give a plating thickness of 20 μm, then followed by the Cu-Sn electrolyte (Starvet) used at 55 °C at a current density of 1.0 amps/dm^2 for 5 minutes for a plating thickness of 1 μm. If required the chromium electrolyte (TriMac III) was plated at 60 °C at a current density of 10 amps/dm^2 for 12 min to give a deposit thickness of 0.3 μm. All pre-treatment solutions and electrolytes are available commercially and were supplied by MacDermid PLC.

The acid copper was plated to give the same overall deposit thickness as the standard nickel and chromium process. The Cu-Sn deposit is not plated commercially above a few microns due to its change in appearance from a silvery bright deposit to a dull grey deposit (which is unsuitable as a nickel replacement). This

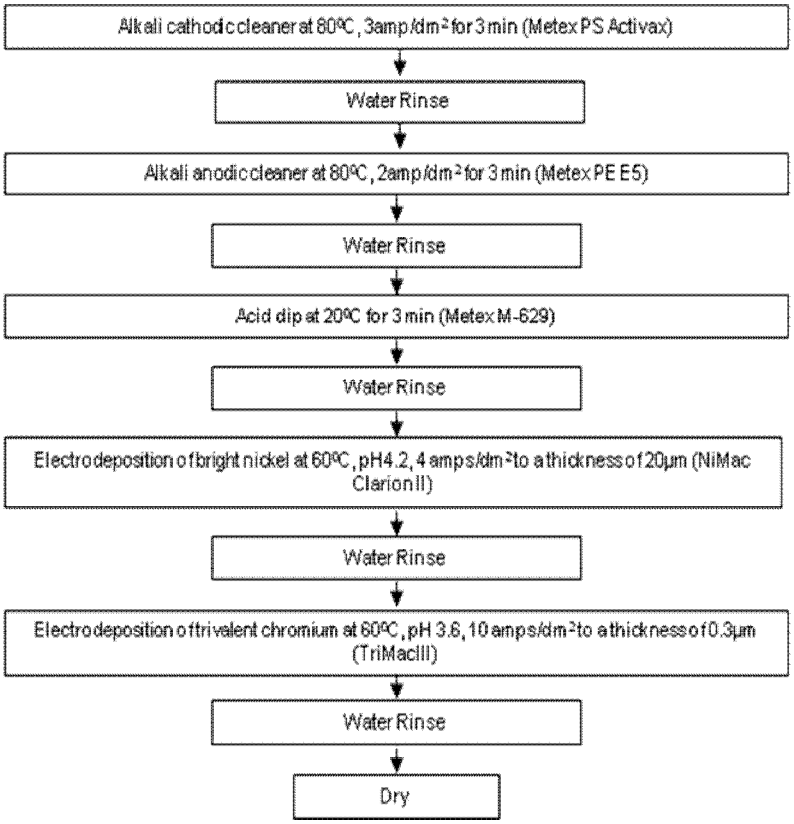

Fig. 1 Process sequence for the electrodeposition of bright nickel and trivalent chromium onto a brass substrate.

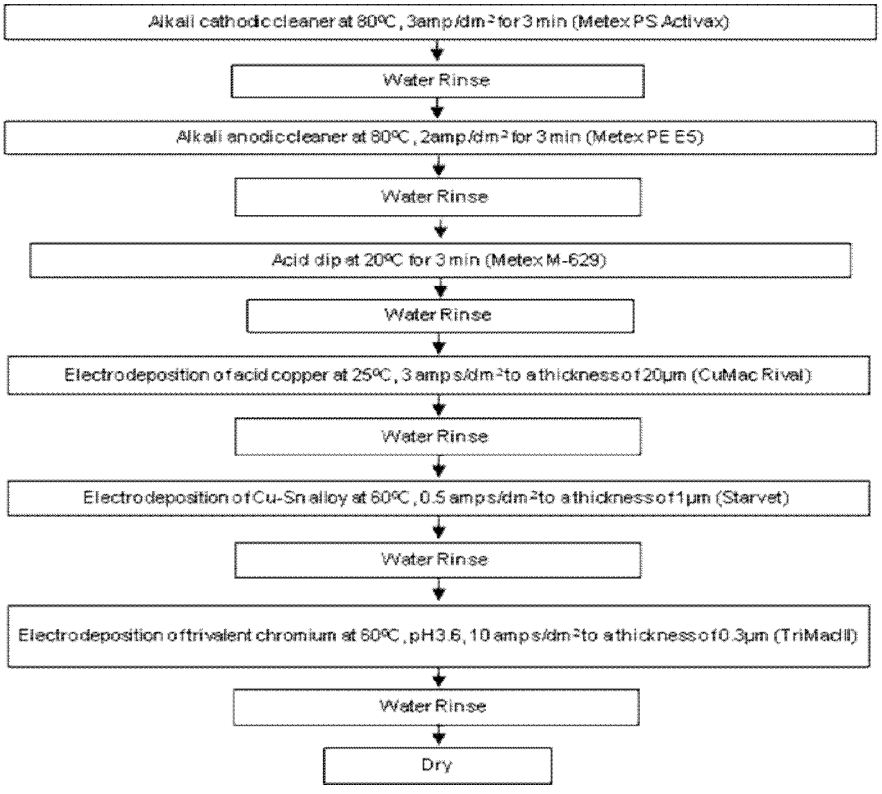

Fig. 2 Process sequence for the electrodeposition of Cu-Sn deposit and trivalent chromium onto a brass substrate.

approach allowed the corrosion testing to be comparable between the two plating sequences as they were of similar overall deposit thickness.

2.2 Colorimetric Analysis

Colorimetric analysis was carried out to determine the colour difference between the deposits. A spectrophotometer (Konica Minolta, model CM-2600d) was used to characterise the colour as a numeric value, therefore allowing a better comparison of colour without it being subjective [24]. The colour is reported using the L*a*b* colour space, which allows an independent evaluation and consistency of results [25]. The readings were taken across the panel to account for high and low current density areas and the average reading taken.

L* indicates lightness of the deposit, the values range from 0-100, the higher the value the lighter the deposit.

a* indicates the red and green colour of the deposit, the values range being between -60 to +60, the more positive the value the more red in colour, while the more negative the value the more green in colour.

b* indicates the yellow and blue colour of the deposit, the values range between -60 to +60, the positive value stands for yellow while the negative value stands for blue.

2.3 Atomic Force Spectroscopy (AFM) Analysis

Atomic force spectroscopy (Veeco Dimension 3100) was used to calculate the roughness of the deposits by using the contact mode technique. This would help identify a more detailed surface characterisation of each deposit as it is able to quantitatively measure the surface roughness to a nanometer scale. Rmax (Eq. (1)) represents the maximum vertical distance between the highest and lowest data points in the same image following the plane fit. RMS (Eq. (2)) is the root mean square average of height deviations taken from the mean image data plane, the roughness calculation (RMS) is simple and most common method for observing any changes in the surfaces topography [26].

$$R_{\max} = \frac{\sum |X - X_0|}{N^0} \quad (1)$$

$$RMS = \frac{\sum (X - X_0)^2}{N^{-1}} \quad (2)$$

where X is the value of heights across the entire image and N is the number of data points. A limitation with using *RMS* algorithm is that it will work with the best fit of all the height points and not the spatial frequency of the features.

2.4 Corrosion Analysis

Two different methods were used to inspect the corrosion performance of the different deposits. The first method was by linear polarisation, an electrochemical method where current is applied 20 mV either side of the open circuit potential. From this the corrosion current (I_{corr}) and corrosion rate in millimetres per year (MPY) can be calculated. The second method is by visual corrosion observed on each sample; this is achieved by putting the samples in a corrosion cabinet and introducing a corrosive atmosphere to accelerate corrosion. This study used two types of corrosive atmospheres, 1) Neutral Salt Spray (NSS) and 2) Copper Accelerated acetic acid Salt Spray (CASS). Each method will be explained in more detail later in this section. Accelerated corrosion methods cannot be related to actual time and is subjective to the individual interpretation, but results are comparative to each other when tested to the same specification and evaluation.

2.4.1 Linear Polarisation Measurements

The corrosion current density I_{corr} was determined by a linear polarisation method using a potentiostat (EG + G Instruments, model 263A). This was carried out in 5% neutral sodium chloride solution using a Ag/AgCl reference electrode over a potential range of +/- 20 mV versus open circuit potential. The 1 cm^2 surface area of the sample was left to equilibrate for 1 h in the NaCl solution. Each panel was analysed five times and the average value was reported. The corrosion current density can be converted to corrosion rate in

millimetres per year (mpy) according to Eq. (3) [27].

$$MPY = I_{corr} (\Lambda) (1/\rho) (\varepsilon) \quad (3)$$

where I_{corr} is the corrosion current density in amps/cm^2, Λ is a combination of several conversion terms and is 1.2866×10^5 [equivalents.sec.ml]/[Coulombs.cm.year], ρ is the metal density in grams/cm^3, ε is the equivalent weight of the metal in grams (equivalent weight is the molecular weight of the metal divided by the number of electrons in the anodic half reaction).

Electrochemical corrosion measurements are used to accelerate the corrosion of the metal by applying a voltage which will push the metal/electrolyte interface beyond its steady state conditions, this causing an electrical current to flow which is measurable. The results can then be interpreted to determine the metallic corrosion behaviour and estimate the corrosion resistance [27].

2.4.2 Neutral Salt Spray (NSS) Corrosion Analysis

A 5% sodium chloride solution was made to ASTM B117 specification (50 g/L sodium chloride, pH adjustment with sodium hydroxide or hydrochloric acid) and operated to the ASTM B117 specification. ASTM B117 specification is a popular standard used by industries such as the aerospace, automotive, military and medical to name a few [28]. The running of the test and evaluation will be standardised by each industry as they set out their own criteria for a pass depending on the level of corrosion protection required. This method is the least aggressive atmosphere out of the two conditions selected.

2.4.3 Copper Accelerated Acetic Acid Salt Spray (CASS) Corrosion Analysis

A salt solution was made to ASTM B368 specification (50 g/L sodium chloride, 0.25 g/L copper chloride, pH adjustment with acetic acid). The corrosion cabinet was operated to the ASTM B368 specification. ASTM B368 was originally developed for chromium electroplating on nickel and chromium/nickel/copper electroplating [29]. It is a more aggressive test than ASTM B117 due to the more acidic environment and the addition of copper to the salt solution.

The corrosion rating for both NSS and CASS is measured according to ASTM B537 specification (standard practice for rating of electroplated panels subjected to atmosphere exposure). The first rating is assigned to the appearance as affected by corrosion of the substrate. A second rating is assigned to the appearance as affected by deterioration of the coating itself.

3. Results

3.1 Colorimetric Results

Comparing the colour difference of the deposits, the Cu-Sn deposit was lighter and bluer than the bright nickel. The chromium deposit was lighter, greener and bluer than the bright nickel and the Cu-Sn deposits. The colour of the chromium deposit remained constant showing the electroplated deposit underneath had little or no effect on the overall colour.

Table 1 shows the L*a*b* values obtained for each panel. For this study, Cu-Sn deposit could not be plated to the same thickness as the bright nickel deposit, since above a few microns, the appearance of the deposit is sacrificed (giving a dull grey/silver deposit). The appearance of this thicker Cu-Sn deposit therefore would not be an acceptable replacement for nickel.

3.2 AFM Results

The AFM results from this study identify the nickel deposit to be the smoothest of all the deposits characterised with an RMS and Rmax values of 3.08 nm

Table 1 Average L*a*b* colour values for electroplated deposits.

Deposit	L*	a*	b*
Bright nickel	83.12	0.81	6.68
Bright nickel + Chromium	82.78	-0.21	0.66
Cu-Sn (1 μm)	86.26	0.40	3.25
Cu-Sn (1 μm) + Chromium	82.89	-0.26	0.93

and 18.6 nm respectively. The Cu-Sn deposit is the roughest of all deposits studied with the following RMS and Rmax values of 8.30 nm and 73.0 nm, respectively. The chromium deposit increases the roughness of the nickel deposit giving RMS and Rmax values of 3.91 nm and 36.6 nm, respectively, but reduces the roughness when plated onto the Cu-Sn deposit with values of RMS 5.60 nm and Rmax 33.7 nm. The acid copper deposit was found to have a RMS value of 5.92 nm and Rmax of 58.5 nm. A thicker Cu-Sn deposit was plated to show that the roughness increased with thickness to give a RMS value of 12.6 nm and Rmax value of 120.0 nm. All results can be found in Table 2 and Figs. 3-8 show the AFM three dimension images of all the deposits plated.

3.3 Corrosion Results

3.3.1 Linear Polarisation Results

Linear polarisation results indicated that whilst Cu-Sn deposit has similar corrosion current density to chromium plated deposit, the bright nickel deposit has a much higher corrosion current density compared to all other deposits. Table 3 shows the corrosion current densities for all panels plated. The corrosion rates show that the chromium deposit with either nickel or Cu-Sn deposit underneath has the slowest corrosion rate of 0.024 and 0.034, respectively. The nickel deposit has the highest corrosion rate of 0.285 mpy compared to all other deposits. From these results it would be expected that the Cu-Sn deposit would show better corrosion resistance in the corrosion cabinets compared to the nickel deposit (this is not the case when evaluating the NSS and CASS) and the chromium deposit would provide the best protection overall (this was supported by the NSS and CASS results). It is important to note that the I_{corr} value is an average corrosion current density of the surface and will not isolate areas of higher and lower corrosion current densities. The following assumptions were made when calculating the corrosion rate:

(1) The alloy composition of the Cu-Sn deposit was 2 copper atoms to 1 tin atom with an average molecular mass;

(2) All deposits were assumed pure for the density value;

(3) All deposits were free from any defects on the surface.

3.3.2 NNS Results

The NSS corrosion cabinet results shown in Table 4 indicate that the bright nickel deposit had no corrosion defects after 24 h but did discolour, after 48 h the deposits appearance deteriorated but still provided protection to the substrate, while after 72 h the bright nickel deposit showed localised corrosion sites in a few areas down to the substrate. The bright nickel/chromium panels showed there were no defects or discolouration to the chromium deposit after 72 h. Inspection of Cu-Sn deposit after 24 h showed the appearance of corrosion sites. As testing continued, the Cu-Sn deposits showed an increasing number of defects to the overall panel and corrosion spots through to the substrate were evident. The Cu-Sn/chromium deposit showed a slight increase in corrosion protection when compared to the Cu-Sn deposit alone. The Cu-Sn/chromium deposit did have increased corrosion defects when compared to the nickel/chromium coatings.

3.3.3 CASS Results

The CASS corrosion cabinet results presented in

Table 2 AFM Roughness Measurements.

Deposit	RMS (nm)	Rmax (nm)
Bright nickel	3.08	18.6
Bright nickel + Chromium	3.91	36.6
Acid copper	5.92	58.5
Cu-Sn (1 μm)	8.30	73.0
Cu-Sn (1 μm) + Chromium	5.60	33.7
Cu-Sn (12 μm)	12.6	120.0

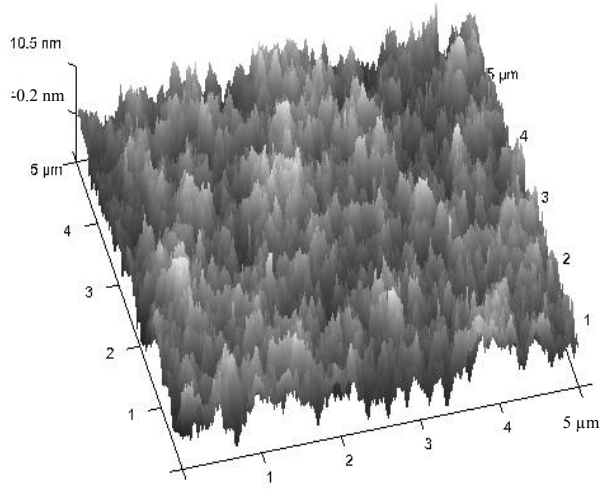

Fig. 3 AFM image of the nickel deposit.

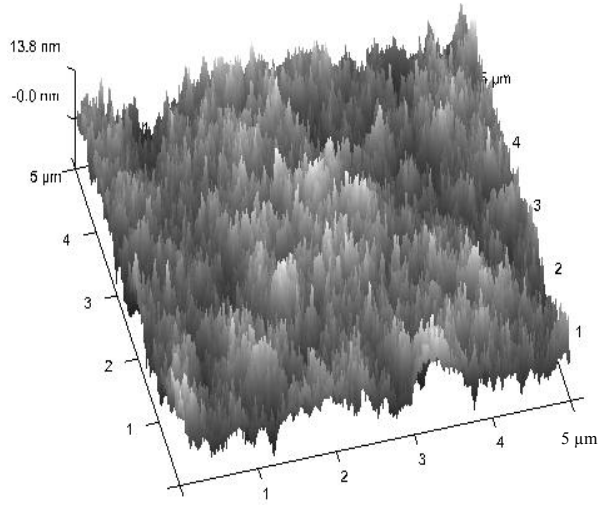

Fig. 4 AFM image of the nickel + chromium deposit.

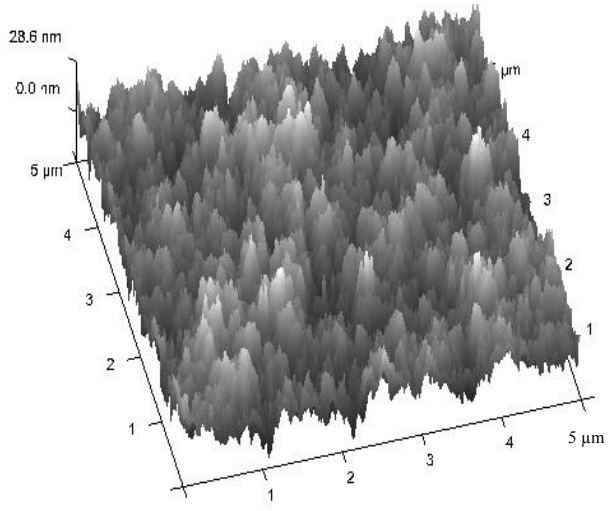

Fig. 5 AFM image of the Cu-Sn deposit (1 µm).

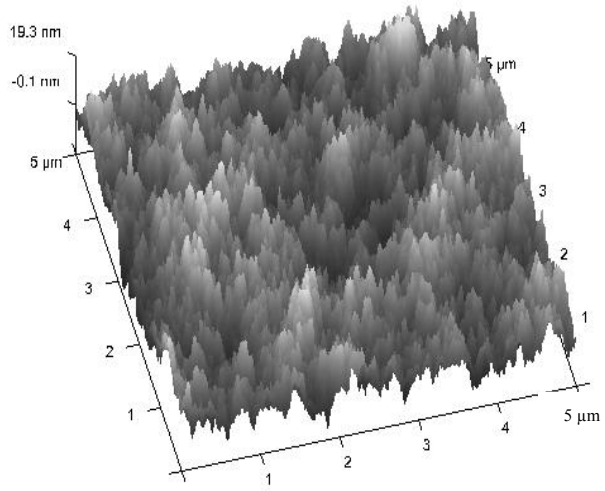

Fig. 6 AFM image of the Cu-Sn deposit + chromium deposit.

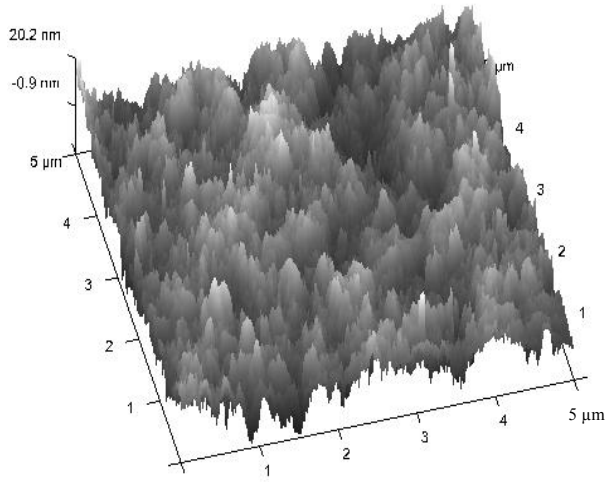

Fig. 7 AFM image of the acid copper deposit.

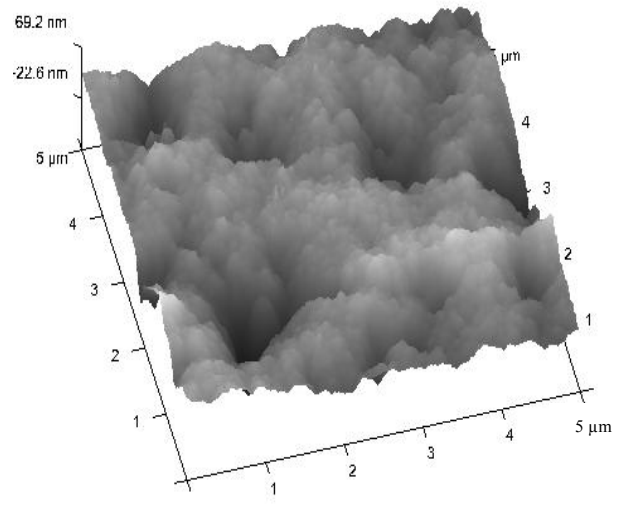

Fig. 8 AFM image of the Cu-Sn deposit (12 µm).

Table 3 Average I_{corr} values for electroplated deposits.

Deposit	Average I_{corr} (nA/cm^2)	Corrosion rate (mpy)
Bright nickel	483	0.285
Bright nickel + chromium	77	0.024
Cu-Sn (1 μm)	197	0.232
Cu-Sn (1 μm) + chromium	108	0.034

Table 4 NSS results (ASTM B117).

Deposit	Rating after 24 h	Rating after 48 h	Rating after 72 h
Bright nickel	10/2	8/2	3/1
Bright nickel + chromium	10/10	10/10	10/10
Cu-Sn (1 μm)	4/4	4/4	3/2
Cu-Sn (1 μm) + chromium	8/8	6/5	4/2

Table 5 CASS results (ASTM B368).

Deposit	Rating after 8 h	Rating after 16 h
Bright nickel	2/2	1/1
Bright nickel + chromium	10/10	10/8
Cu-Sn (1 μm)	4/4	4/4
Cu-Sn (1 μm) + chromium	6/6	5/5

Table 5 established that the bright nickel deposit provided the least corrosion protection compared to all other deposits, while chromium plated onto bright nickel deposit provided the best corrosion protection. The nickel/chromium deposit after 8 h showed no visible corrosion sites, after 16 h small corrosion sites in the chromium deposit were starting to form. The inspection of the Cu-Sn deposits after 8 h showed the corrosion had spread evenly over the panel, while after 16 h the Cu-Sn deposit had not corroded as fast as the nickel deposit. The chromium plated onto the Cu-Sn deposits did improve the corrosion protection compared to only the Cu-Sn deposit alone, although corrosion sites were still visible. Overall, the chromium deposit provided better corrosion protection when plated on top of bright nickel compared to being plated onto Cu-Sn deposit. When evaluating accelerated corrosion results such as in NSS and CASS, it is not possible to relate the results to actual corrosion performance. It can only be used as a comparison to other deposits that have undergone the same test.

4. Discussion

The Cu-Sn deposit plated to a thickness of 1 μm to obtain a bright silver finish is achieved by the bright copper substrate; the brightness of the copper penetrates through the thin Cu-Sn deposit giving it the required bright finish, similar to that of nickel. The chromium plated over either nickel or the Cu-Sn deposit shows little variation in colour, this proving the Cu-Sn deposit could replace nickel in terms of appearance. The thicker Cu-Sn deposit showed increased roughness when plated to 12 μm, thus scattering the light more and therefore the deposit appears dull and not comparable to the appearance of the nickel deposit. This concludes that there is a limit to the thickness the Cu-Sn can be plated. The thinner Cu-Sn deposit however has the disadvantage of it being porous; as a consequence the corrosion protection is reduced. The contradicting results of the linear polarisation and corrosion cabinet tests highlight the pores in the Cu-Sn deposit. The electrochemical test indicate that the Cu-Sn deposit provides more corrosion protection than the nickel deposit so therefore should be confirmed by the accelerated corrosion testing, however, as highlighted previously the results actually contradict each other. This can be explained by the Cu-Sn deposit being porous, the pores

in the deposit allow a corrosion path to the substrate and therefore not providing much in terms of corrosion protection (this was seen by the localised corrosion sites on the panels). The linear polarisation does not take into account of any surface defects or impurities of a deposit and therefore didn't highlight the pores.

Bright nickel deposits plated to a thickness of 20 μm are not porous, this is shown by accelerated salt spray tests indicating localised corrosion sites. These sites tend to start where the deposit has a defect and therefore not spread evenly over the deposits surface. Pores however are spread evenly throughout the deposit and therefore a distinction between the two can be made. The difference seen between the nickel deposit and the Cu-Sn deposit was that the nickel deposit showed only a few localised corrosion sites which increased in size with continued exposure to the salt solution, where the Cu-Sn deposit had numerous but smaller corrosion sites all over the panel surface.

The chromium deposit is also porous similar to Cu-Sn as it is only plated to 0.3 μm. As the pores are distributed evenly over the chromium surface, it is less likely that there would be localised corrosion sites as seen with the nickel deposit. The smaller areas of corrosion, which will start at a pore, are distributed evenly over the chromium surface and therefore provide a more aesthetically appealing deposit as it starts to corrode. The porous chromium deposit works well with a non-porous nickel deposit underneath as the corrosion can spread under the chromium deposit but not penetrate through the nickel to the substrate so fast, as shown by the corrosion ratings given to the nickel/chromium deposit compared to the Cu-Sn/chromium deposit. The porous Cu-Sn deposit provides a path for the corrosion to penetrate to the underlying coating in this case it is the acid copper. The idea was that the copper would provide the same non-porous layer as the bright nickel deposit, but although the copper deposit is non-porous it corrodes faster than the nickel so the corrosion starts becoming visible over the whole deposit, thus compromising the overall appearance of the deposit.

Once the deposits are exposed to 16 h CASS or 72 h NSS it is seen that there is little difference between the Cu-Sn and bright nickel deposit, thus demonstrating that corrosion as soon as it has been established whether localised or evenly distributed over the surface, eventually the deposit reaches a level where corrosion becomes clearly visible. Overall, the best protection against corrosion is the widely used bright nickel/chromium deposit as it outperforms all the other deposits tested in this study.

5. Conclusions

The objective of this study was to characterise a Cu-Sn deposit and determine if it was a practical alternative to the nickel layer under decorative chromium. On the basis of this study the following conclusion was reached. The Cu-Sn deposit could replace the nickel layer under chromium to produce an acceptable appearance but it could not match the same corrosion performance as the nickel deposit under chromium; therefore the Cu-Sn deposit would not be a suitable replacement for the nickel deposit where corrosion protection is primary. Other conclusions drawn from this study are as follows:

(1) The colour of the chromium deposit does not vary greatly when plated on to either Cu-Sn deposit or bright nickel deposit;

(2) The Cu-Sn/chromium deposits do not provide the same level of corrosion protection as nickel/chromium deposits;

(3) The corrosion rate of the Cu-Sn deposit is lower than bright nickel indicating that it could provide better corrosion protection to the substrate if the deposit was not porous;

(4) Cu-Sn deposit will not replace nickel where corrosion protection is required;

(5) Cu-Sn/chromium deposits have the potential to replace nickel/chromium deposits where used primarily for cosmetic appearance and in a moderately corrosive atmosphere.

Acknowledgments

The authors wish to show their gratitude to the EPSRC, Kohler-Mira PLC and MacDermid PLC for the sponsorship of this project and also MacDermid PLC for the use of their chemicals and equipment. S.L. Handy would like to thank the School of Engineering and Built Environment, University of Wolverhampton for their support during the course of this study.

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